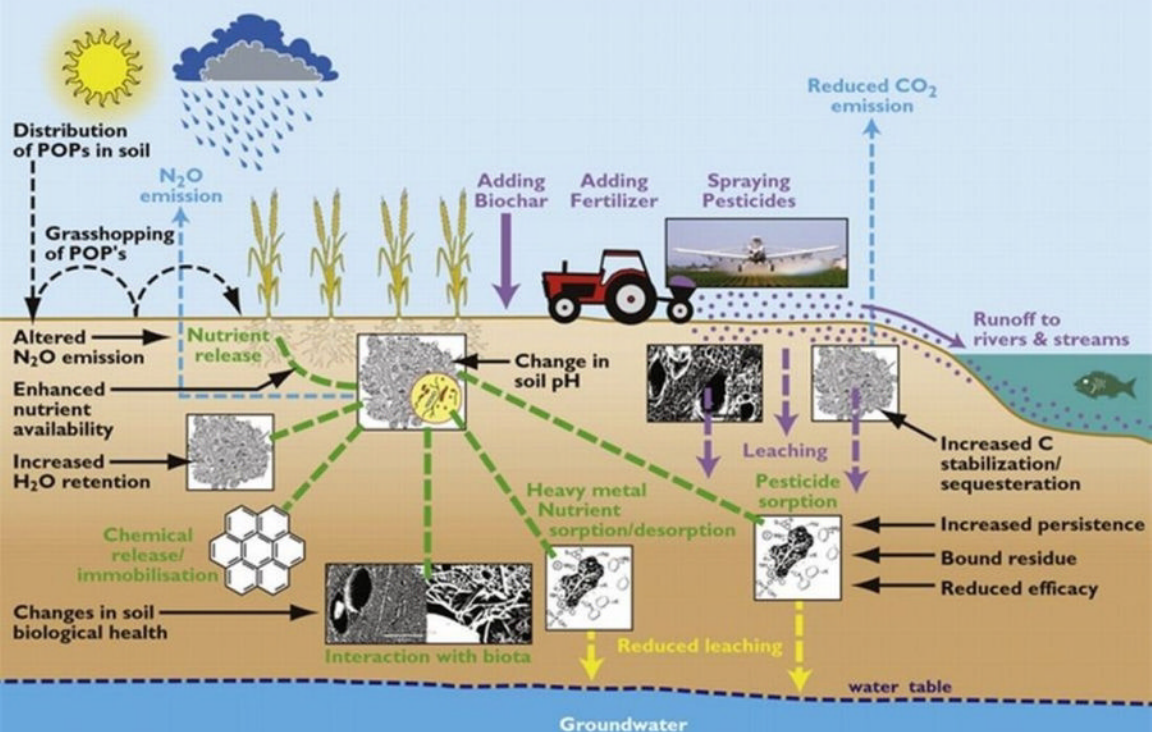
Volume 112

Advances in Agronomy



AP

VOLUME ONE HUNDRED TWELVE

ADVANCES IN AGRONOMY

ADVANCES IN AGRONOMY

VOLUME ONE HUNDRED TWELVE

ADVANCES IN AGRONOMY

EDITED BY

DONALD L. SPARKS

Department of Plant and Soil Sciences
University of Delaware
Newark, Delaware, USA



AMSTERDAM • BOSTON • HEIDELBERG • LONDON
NEW YORK • OXFORD • PARIS • SAN DIEGO
SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO
Academic Press is an imprint of Elsevier



Academic Press is an imprint of Elsevier
525 B Street, Suite 1900, San Diego, CA 92101-4495, USA
225 Wyman Street, Waltham, MA 02451, USA
32 Jamestown Road, London, NW1 7BY, UK
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands

First edition 2011

ISBN: 978-0-12-385538-1
ISSN: 0065-2113 (series)

For information on all Academic Press publications
visit our website at elsevierdirect.com

Printed and bound in USA
11 12 13 14 10 9 8 7 6 5 4 3 2 1

Contents

CONTRIBUTORS

Numbers in Parentheses indicate the pages on which the authors' contributions begin.

Randy L. Anderson (205)
USDA-Agricultural Research Service, Brookings, South Dakota, USA

Roland Bol (1)
Rothamsted Research, North Wyke, Okehampton, Devon, United Kingdom

Nanthi S. Bolan (145)
Centre for Environmental Risk Assessment and Remediation (CERAR), and Cooperative Research Centre for Contaminants Assessment and Remediation of the Environment (CRC CARE), University of South Australia, Adelaide, Australia

David Chadwick (1)
Rothamsted Research, North Wyke, Okehampton, Devon, United Kingdom

Keun Young Huh (145)
Department of Landscape Architecture, Gyeongnam National University of Science and Technology, Dongjin-ro 33, Jinju, Gyeongnam, Republic of Korea

R. S. Kookana (103)
CSIRO Land and Water, Sustainable Agriculture Research Flagship, Glen Osmond, South Australia, Australia

E. Krull (103)
CSIRO Land and Water, Sustainable Agriculture Research Flagship, Glen Osmond, South Australia, Australia

Ravi Naidu (145)
Centre for Environmental Risk Assessment and Remediation (CERAR), and Cooperative Research Centre for Contaminants Assessment and Remediation of the Environment (CRC CARE), University of South Australia, Adelaide, Australia

Jin Hee Park[1] (145)
Centre for Environmental Risk Assessment and Remediation (CERAR), and Cooperative Research Centre for Contaminants Assessment and Remediation of the Environment (CRC CARE), University of South Australia, Adelaide, Australia

[1] Current address: Centre for Mined LandRehabilitation (CMLR), University of Queensland, Brisbane, Australia

Brett Robinson (145)
Department of Soil Science, Lincoln University, Lincoln, New Zealand

A. K. Sarmah[2] (103)
Soils and Landscape Responses Team, Landcare Research Manaaki Whenua, Hamilton, New Zealand

Anita Shepherd (1)
Rothamsted Research, North Wyke, Okehampton, Devon, United Kingdom

B. Singh (103)
Faculty of Agriculture, Food and Natural Resources, The University of Sydney, Sydney, New South Wales, Australia

Mervin St. Luce (55)
Department of Natural Resource Sciences, Macdonald Campus of McGill University, Ste-Anne-de-Bellevue, and Soils and Crops Research and Development Centre, Agriculture and Agri-Food Canada, Quebec City, Quebec, Canada

L. Van Zwieten (103)
Department of Primary Industries, Wollongbar, New South Wales, Australia

Joann K. Whalen (55)
Department of Natural Resource Sciences, Macdonald Campus of McGill University, Ste-Anne-de-Bellevue, Quebec, Canada

Lianhai Wu (1)
Rothamsted Research, North Wyke, Okehampton, Devon, United Kingdom

Bernie J. Zebarth (55)
Potato Research Centre, Agriculture and Agri-Food Canada, Fredericton, New Brunswick, Canada

Noura Ziadi (55)
Soils and Crops Research and Development Centre, Agriculture and Agri-Food Canada, Quebec City, Quebec, Canada

[2] Current address: Faculty of Engineering, University of Auckland, New Zealand

Preface

Volume 112 contains five informative reviews that address globally important areas in the crop and soil sciences. Chapter 1 is a comprehensive review of models to simulate the impacts of climate change and adaptation–mitigation management practices on water pollution and emissions of greenhouse gases. Chapter 2 addresses measurements to determine the dynamics of mineralizable nitrogen in humid tropical soils. Chapter 3 covers the pros and cons of using biochar to sequester carbon and enhance crop production. Chapter 4 discusses numerous aspects of phytostabilization for mitigating soils contaminated with metal(loid)s. Chapter 5 covers synergism in crops and impacts on growth efficiency.

I appreciate the excellent contributions of the authors.

Donald L. Sparks
Newark, Delaware, USA

CHAPTER ONE

A Review of Quantitative Tools for Assessing the Diffuse Pollution Response to Farmer Adaptations and Mitigation Methods Under Climate Change

Anita Shepherd, Lianhai Wu, David Chadwick, *and* Roland Bol

Contents

Abstract

In an era of global climate change, the agricultural sector faces the challenge of increasing the production of safe and nutritious food supplies to meet a growing world population while safeguarding the environment. Farmers will adapt their agricultural practices to a changing climate to safeguard against loss of production and to take advantage of any positive climatic conditions. Certain management practices have been found to reduce the effects of agricultural practices on the environment and a key question is how efficient these are under the current climate, and will these management practices still be relevant under a changing

Rothamsted Research, North Wyke, Okehampton, Devon, United Kingdom

Advances in Agronomy, Volume 112
ISSN 0065-2113, DOI: 10.1016/B978-0-12-385538-1.00001-9

climate? Mathematical modeling is the only tool available to assess the potential efficacy of proposed agricultural management practices to help evaluate their impacts on the environment in a future climate. This chapter attempts to evaluate a range of published models for their capability to simulate agricultural production systems and associated environmental system losses under a changing climate, and their ability to introduce farmer adaptation and mitigation methods. The chapter focuses on the applicability of the models given a set of essential criteria related to scale, biophysical processes, and land management. Thirty models are initially examined, based on details found in published papers, against specific criteria, viz: (1) spatial scale and temporal scale, ease of use, and ability to consider a change in climate; (2) ability to simulate nutrient cycling processes, specifically carbon and nitrogen dynamics with microbial turnover, mineralization–immobilization, nitrification and denitrification, plant nutrient uptake, and phosphorus cycling; (3) ability to consider a water balance and water movement through soil; and (4) ability to introduce and modify agricultural practices relating to crop and livestock management. The chapter does not compare any actual model simulations. It was concluded that albeit no single model incorporates all above stated requirements, there were three models, DAYCENT, PASIM, and SPACSYS which will accommodate most features. These models may therefore be considered in the context of this chapter to be the most suitable for a general assessment of the effects of farm mitigation and adaptation on environmental losses under a changing climate.

1. Introduction

1.1. Safeguarding the environment

There is a need to increase agricultural production while safeguarding the environment (Defra, 2009; Horrigan *et al.*, 2002; Morris and Winter, 1999), and this challenge is set in the era of a changing climate. It is clear that previous and current agricultural practices impact adversely on a number of ecosystem services (Beman *et al.*, 2005; Pilgrim *et al.*, 2010; Van Wesemael *et al.*, 2010) including water and air quality. For example, agriculture is a major source of phosphorus (P) to the aquatic environment (Granger *et al.*, 2007; Hawkins and Scholefield, 1996; Lewis and McGechan, 2002), hence future research directions will need to better link P losses with soil nutrient and moisture conditions, ecological effects, and climate change (Blackwell *et al.*, 2010; Kronvang *et al.*, 2009; Turner and Haygarth, 2001). Diffuse nitrogen (N) loss from agriculture is also a major contributor to the aquatic environment, in the form of nitrate (NO_3^-) in surface and groundwater (Bust and Haycock, 1993; Froschl *et al.*, 2008; Lerner and Harris, 2009; Ryden *et al.*, 1984). In addition, the processes of nitrification and denitrification are responsible for gaseous emissions of nitrous oxide (N_2O; Cardenas *et al.*, 2010; DeBusk *et al.*, 2001), while methanogenesis in ruminant livestock and livestock manures is responsible for methane (CH_4)

emissions (DeRamus *et al.*, 2003; Matthews *et al.*, 2006; Pinares-Patino *et al.*, 2007). These are two key greenhouse gases (GHGs) whose production is enhanced under intensive agricultural production (Beauchemin *et al.*, 2010; Millar *et al.*, 2010). Both management and environmental factors influence the rates of N_2O and CH_4 emissions from the range of agricultural sources (Del Prado *et al.*, 2010; Meijide *et al.*, 2010; Pereira *et al.*, 2010). Current studies are investigating the potential influence of nutrient amendments to agricultural soils such as compost from food waste and agricultural residuals such as straw (Suntararak, 2010).

Agriculture is also a major emitter of ammonia (NH_3; Cooter *et al.*, 2010; Misselbrook *et al.*, 2001; Nunez *et al.*, 2010), which represents an agronomic loss of N; is associated with N deposition, soil acidification and loss of general biological biodiversity (Fraser and Stevens, 2008); and is also a precursor of fine particulate matter, considered a public health threat (Shih *et al.*, 2006).

Current legislation and advice tries to mitigate diffuse water pollution from agriculture by promotion and adoption of good management practice (Monteny *et al.*, 2006; Van Der Meer, 2008). Agricultural diffuse pollution and soil degradation have led to a reconsideration of agricultural policies in Europe (Collins and McGonigle, 2008). For example, farm income support payments are now linked to compliance with standards (cross compliance rules) to protect the environment and animal health. In addition, the Water Framework Directive (WFD) represents a major effort toward the conservation and management of aquatic ecosystems (Basset, 2010). The Directive runs concurrently with a European Nitrates Directive, to reduce or prevent water pollution caused by NO_3^- from agricultural sources (WFD-UKTAG, 2001). Nitrate vulnerable zones are designated areas of land draining into waters polluted by NO_3^- from agriculture, and farmers with land in NVZs have to follow a mandatory action plan to tackle NO_3^- loss from agriculture.

Major emitters (such as China and the United States) of GHGs have agreed under the Copenhagen Accord that global average temperature increase should be kept below 2 °C (Ramanathan and Xu, 2010). Temperature increases have been linked to an increase in global soil respiration, indicating an acceleration of the carbon cycle (Bond-Lamberty and Thomson, 2010). Actions to stabilize carbon dioxide (CO_2) concentration below 441 ppm during this century, targeting applicable air pollution laws and reducing greenhouse emissions of short-lived CH_4 and hydrofluorocarbons, can reduce the probability of exceeding the 2 °C barrier before 2050 to less than 10%. Specific targets to reduce GHGs and NH_3 emissions have also resulted in a range of agricultural practices to limit emissions, for example, shallow injection of slurry and slurry store covers to reduce NH_3 emissions; supporting biogas production on farms (Regina *et al.*, 2009); techniques to improve carbon sequestration (Lal, 2010); improving the performance of ruminants; regulating the ruminal fermentation; and reducing the emission of GHGs from feces (Li *et al.*, 2010).

1.2. Tools to support agroenvironmental legislation

Nutrient cycling in agricultural systems is complex, and it is important that any potential secondary effects of introducing a mitigation method to reduce pollution are understood. There is a risk that the mitigation method used may stimulate a different form of pollution from another component of the nutrient cycle. There is the potential to either reduce another form of pollution at the same time (a "win–win" situation) or possibly to increase another form of pollution (i.e., "pollution swapping"; Stevens and Quinton, 2009b). However, it is increasingly evident that no single mitigation option will reduce all pollutants (Stevens and Quinton, 2009a).

Stressors of changing climate, land use, and demands on water resources, and their resulting effects on nutrient cycles are predicted to increase over the coming decades (Heathwaite, 2010). Future climate scenarios for the UK predict wetter winters and hotter, drier summers than the historical baseline UK climate (Malby *et al.*, 2007; Mills, 2005; Palmer and Ralsanen, 2002; Vidal and Wade, 2008). It is important to predict the impact of our current thinking of climate change mitigation, in a whole-system context, on gaseous emissions and water loss. For example, what are the physical effects of wetter winters and more intense rainfall events on diffuse water pollutants (Granger *et al.*, 2010b), and will current mitigation advice be adequate, that is, use of buffer strips, cover crops, etc.? (Stevens and Quinton, 2009a) What will be the impacts of hotter, drier summers on preferential flow and losses of diffuse water pollutants or on NH_3 volatilization and N_2O emissions, and will current mitigation advice still be effective? The effects of changed temperature and rainfall patterns and increased atmospheric CO_2 concentrations on nutrient cycling (e.g., nitrification, denitrification, mineralization) and effects on gaseous emissions, diffuse water pollution and, importantly, crop nutrient uptake and yields will be complex.

Agriculture involves a high degree of management but is still susceptible to failure under extremes in weather. As such, there is a need to continuously evaluate farming practices and implement those that minimize adverse effects of weather and take advantage of conditions that promote production and food quality, that is, adaptation. With the likelihood of climate change, agricultural practices will require adaptation to meet the new climate constraints on food production (McGinn and Shepherd, 2003). In addition to mandatory regulations, farmers will naturally adapt their land management to mitigate the effects of a change in climate (Gifford *et al.*, 1996). To determine what current legislation and advice to reduce diffuse pollution to air and water is sufficient to cope with the potential effects of climate change, simulation modeling is required because it has the potential to integrate the complexity of the system, provide a quantitative insight of the direction of change in a flux that occurs as a result of the perturbation of the system, and help to determine the potential outcomes of climate change

on agricultural productivity and effects on the environment (Giltrap *et al.*, 2010; Janzen *et al.*, 2006; Pattey *et al.*, 2007).

1.3. Reviewing the tools to fit the purpose

Although there have been a number of nutrient model reviews for agroecosystem applications and climate (Bryant and Snow, 2008; Challinor *et al.*, 2009; Kersebaum *et al.*, 2007; Lewis and McGechan, 2002; Parton, 1996; Smith *et al.*, 1997), only a limited number or those dealing with single matter cycling models were involved in the reviews. The purpose of this chapter is to determine the strengths and weaknesses of a range of international models (Table 2a and b), based on characteristics essential and desirable in a model (Table 1) to evaluate the adaptation of farming practices to mitigate diffuse pollution under climate change, specifically, the models' ability to simulate the direct effects of climate change on agricultural productivity at the field or farmscale for a range of crop types, environmental losses to water and air, as well as their ability to introduce farmer adaptation and specific mitigation methods. However, we do not undertake any actual performance test or compare accuracy of the model outputs in this chapter. The chapter focuses solely on the applicability of models to meet a given set of essential criteria:

- **(i)** to be able to operate at appropriate spatial and temporal scales;
- **(ii)** to be capable of simulating the processes, transformations, and losses relevant to climate change impacts on agriculture;
- **(iii)** to have capability to simulate and evaluate mitigation methods (e.g., a tool kit for diffuse pollution), and enable examination of potential secondary effects (e.g., win–win and pollution swapping);
- **(iv)** to be able to simulate the effects on outputs resulting from farmer adaptations; and
- **(v)** to have ease of use for the operator.

Ideally, these models should be at farm or field scale to reflect management decisions on farms and for policy; a minimum of a monthly timestep is necessary to reflect management decisions and the cropping calendar.



2. Rationale for Selection of Model Criteria

2.1. General selection

Before any model was chosen for the chapter, we have limited our scope of model selection: first, this chapter is not trying to be exhaustive, only those that have been commonly cited or proven and validated in the literature will be included. And second, our particular focus is on a farming application as well as nutrient cycling and environmental losses. There are an infinite

Table 1 Selection criteria of processes

Criteria	Climate change	Nutrient cycling	Water	Agricultural management
Essential	• Temperature • Precipitation	• Mineralization • Immobilization • Nitrification • Denitrification • C and N dynamics with microbes • Root and shoot partitioning and uptake	• Water balance • Movement through soil layers (i.e., leaching)	• Crop type and timing of agronomic factors • Land-use change • Livestock grazing/housing periods • Fertilizer and manure application, timing, and rates
Desirable	• Fixed/actual weather file input • Atmospheric CO_2 concentrations	• Phosphorus nutrient concentration in streamflow	• Runoff • Sedimentation	• Tillage and physical modification • Modification of animal diet

number of environmental applications that models are written for. The models that fall outside our focus will be excluded in the chapter.

Availability of model details is a recurring problem previously commented on in papers (Tiktak and Vangrinsven, 1995). The documentation of models is the last phase in model building, and sometimes a detailed description of a model in an institute report is a difficult thing to find, even though the model itself may be well known. Lack of details can render models unusable to wider research groups other than their creators (Landsberg *et al.*, 1991), and a model could be overlooked that has a greater capability than is documented, and prevent the model from being more widely used.

In order to select models, we have built on previous reviews (Lewis and McGechan, 2002; Smith *et al.*, 1997), added more recently published papers on appropriate models and added relevant new models not included in these reviews. This chapter is to be used to enable readers to select the most applicable computer model for projects concerning an evaluation of the effectiveness of agricultural practices resulting from farmer adaptation. It is also to be used to enable readers to select the most applicable model for examination of the necessary mitigation methods for various crops as a response to a change in climate, with relevance to productivity and environmental losses.

A list of models used and sources are summarized in Tables 2a and b.

We have separated model *characteristics* into two main levels for this chapter, that is, desirable and essential (Tables 1 and 2a, b; Sections 2.2–2.5). We also consider three other aspects of models which influence their use and application, that is, ease of usage (Section 2.6), spatial scale, and temporal time step (Section 2.7). Processes, transformations, and losses simulated are dealt with in Sections 2.2–2.4. Usefulness of models for diffuse pollution, pollution swapping, and farmer adaptation is dealt with in Section 2.5. Appendix contains brief descriptions of each model included in this chapter along with key descriptive publications, hence these same references after each model are not generally given unless the information was taken from a separate source.

Which model is eventually most applicable will depend largely on what results are expected as output, and therefore processes needed, and for this we need to define some rules to place relative importance on processes. If our focus is on the sustainability of agriculture with adaptation and mitigation under climate change, it may be seen in terms of its resulting pollution, hence the need for a model including processes relating to nutrient loss and pollution. In case models do not include all processes, we must decide which processes take most priority to include in a model. One important source of agricultural pollution is nitrogen. Its output from the soil is in the detrimental forms of NO_3^- and ammonium (NH_4^+) into a watercourse (Granger *et al.*, 2010a; Lu *et al.*, 2009), and N_2O and NH_3 emitted into the

Table 2 Characteristics of reviewed models

(a)

			Resolution		Processes, transformations, losses relevant to climate change									
					Losses to waters					Atmospheric losses				
ID	Models	Characteristics, focus of model	Spatial	Temporal	Leached N	Runoff N	P	Sediments	Fecal/ pesticides	NH_3	N_2O	NO	CH_4	Transformations in soil
1	ANIMO	A nutrient model strong on manure and slurry components	Field scale, 50 soil layers	Daily–weekly	y	Y	Leaching, surface dissolved runoff			y	Gases treated as one sink			Decomposition, nitrification, denitrification, min/immobiliz (P, N), P soil sorption/ desorption, C dynamics
2	APSIM	Crop production, N and C cycling, water	Field scale	Daily	y			Soil erosion			Gases treated as one sink			Decomposition, min/immobiliz, nitrification, denitrification
3	BASINS	Water quality and erosion model; open GIS tool with web dataset	Catchment	Daily	y	Y		Soil erosion						
4	CNSP Pasture	A pasture uptake model	Field	Monthly	y	Y								
5	PASIM	Mechanistic pasture simulation model	Field scale, one-dimensional	Daily	y	Y		Soil erosion	Pesticides	y	y	y		Net mineralization, nitrification, denitrification, and NH_4 sorption
6	DAISY	Crop, C and N and water flows with heat balance and land management	Field scale, over 20 layers, one-dimensional	Daily	y	Y			Pesticides		Gases treated as one sink			Min/immobiliz, nitrification, and denitrification

7	DAYCENT (daily version of CENTURY)	Rainfall, temperature, NH_4 simulated within 15 cm on the top soil	Field scale, 10 soil layers, one-dimensional	Daily	Leaching (P)		Leaching, surface dissolved runoff	P erosion			y	y	y	Decomposition, nitrification, denitrification (N) min/immobiliz (P, N), P soil sorption/desorption, C dynamics
8	ECOSYS	Complex integrated terrestrial system	Various scales (field to km)	Hourly to centuries						y	y	y	y	Decomposition, nitrification, denitrification, Min/immobiliz (P, N), C dynamics
9	EUROSEM	Erosion model of sediment transport, potential to be coupled with an agricultural P cycling model	Catchment	Short-term			Soil erosion	Sediment transport						
10	EVENFLOW	Complex stream N model	Catchment	Daily	y									No separate processes, empirical from experimental nitrate data
11	GLEAMS	Nonpoint source stream loading, P, uptake of NO_3	Field scale 10 soil layers	Daily	y	Y	Leaching, surface dissolved	P bound to particulate, detachment + transport	Pesticides	y	Gases treated as one sink			Decomposition, nitrification, denitrification, min/immobiliz (P, N), P soil sorption/desorption

(*Continued*)

Table 2 (*Continued*)

(a)

ID	Models	Characteristics, focus of model	Resolution: Spatial	Resolution: Temporal	Processes, transformations, losses relevant to climate change — Losses to waters: Leached N	Runoff N	P	Sediments	Fecal/ pesticides	Atmospheric losses: NH_3	N_2O	NO	CH_4	Transformations in soil
12	HURLEY	Pasture growth and soil nutrient cycling	Field	Hour										C cycling, plant N uptake, nitrification and denitrification, min/immobiliz (N)
13	INCA	Process-based N cycle in plant–soil-stream loading, macro- and micropore drainage	Catchment	Daily	NO_3^-, NH_4^+, separate for soil water and groundwater					Since nitrification and denitrification included, no gaseous output, a wasted opportunity				Plant uptake, nitrification and denitrification, min/immobiliz (N), matrix and macropore soil drainage
14	MACRO	Water pollution, 2-domain with macro- and soil matrix micropores	Field scale, 15 soil layers	Daily–hourly or less			Colloid + soluble, bound to particulate		Pesticides					Not a C/N cycling model
15	MONERIS	Point and diffuse streamflow loading	Catchment	Annual	y	Y								Conceptual approach, no detailed processes
16	MOTOR	A unique, flexible SOM framework for interchangeable processes based on reaction kinetics	Expressed as mass, flexible units	Daily										Based on pools and fluxes, does not explicitly name processes

17	NGAUGE	Detailed N cycling	Field scale	Monthly	y					y	y	y		Decomposition, min/immobiliz, nitrification, denitrification
18	NOPOLU	Nutrient loss to surface water	Catchment	Annual		Y								No soil processes
19	OVERSEER	Livestock management model	Farm	Annual										
20	PSYCHIC	Phosphorus flow, not stream routing	Field/Catchment	Monthly										
21	REALTA	Nutrient loss to surface water	Catchment	Annual	y	Y	y							No soil processes
22	RZWQM	Tillage, macropore transport	Field scale, up to 10 soil layers	Daily	y	Y		Soil erosion	Pesticide, fecal	y	y	y		Decomposition, min/immobiliz, nitrification, denitrification, C dynamics
23	SIMSDAIRY	Detailed farm N cycling	Farm (dairy)	Monthly	y		y	y		y	y	y	y	
24	SOIL + SOILN	An integrated C/N dynamics model	Field scale, number of soil layers depends on soil simulation, can have over 20	Daily	y	Y					Gases treated as one sink			Decomposition, min/immobiliz, nitrification, denitrification (all N gases included)
25	SOMM	Specialized SOM mineralization and humification	Plot to global	Long-term										Decomposition, nitrification, denitrification, N release

(*Continued*)

Table 2 (*Continued*)

(a)

					Processes, transformations, losses relevant to climate change									
			Resolution		Losses to waters					Atmospheric losses				
ID	Models	Characteristics, focus of model	Spatial	Temporal	Leached N	Runoff N	P	Sediments	Fecal/ pesticides	NH_3	N_2O	NO	CH_4	Transformations in soil
26	SOURCE AP			Annual										Simplistic, no soil processes
27	SPACSYS	Flexible, integrated plug-and-play nutrient model for plant, roots, agricultural management	Field scale, layers flexible	Daily	y	Y			Fecal		y	y		Decomposition, min/immobiliz, nitrification, denitrification
28	MODCOU	Hybrid spatial scales	Modcou regional scale (and plot-scale version-STICS)	Daily	y	Y					Gases treated as one sink			Decomposition, net mineralization, nitrification, denitrification
29	SUNDIAL/ MAGEC	Crop and Nutrient flow	Four fixed layers, field output	Monthly/ daily	y					y	Gases treated as one sink			Decomposition, min/immobiliz, nitrification, denitrification
30	UK-DNDC/ DNDC	Integrated C/N dynamics with crop growth	Plot, regional	Daily	Attempted but not well-developed water module					y	y	y	y	Decomposition, nitrification, denitrification, plant growth, ammonia volatilization

(b)

ID	Models	Processes, transformations, losses relevant to climate change				Pollution Swapping (C, N, P)	Mitigation	Farmer adaptations	Limitations	Source of info (see references in full)
		Plant		Hydrology	Other					
		Climate	Shoot:root							
1	ANIMO	Soil temperature, saturated and unsaturated systems, ground and surface water		Field drains, lateral, vertical, saturated/unsaturated, groundwater and surface water	Natural areas, forest, wetland plant types	C dynamics	Manure, fertilizer	Different crops, grazing	No N_2O, focuses on leached nutrients	Groenendijk and Kroes (1999), Schoumans and Silgram (2003)
2	APSIM	Plant water uptake, soil temperature, water	Active uptake, mass flow, diffusion to roots	Vertical drainage		C dynamics module			Originally developed for sugarcane, other crops need to be developed	Huth *et al.* (2010), Shaffer and Ma (2001)
3	BASINS	Takes in hydrological data from GIS including future climate projections		Strong in catchment flows					Not agricultural management, limited US web-based geo-related dataset	Mohamoud *et al.* (2009)
4	CNSP Pasture	Soil temperature, water	Root length and uptake; alter ratio if deficient; mycorrhizal effects	Soil water dynamics affecting C/N dynamics		C dynamics	Fertilizer		No N_2O; no separate SOM decomposition pools	McCaskill and Blair, 1990
5	PASIM	Plant uptake, soil water dependent, temperature, microclimate submodel	Partitioning between shoot:root; root uptake and exudation	Vertical percolation	Physiological effects of CO_2 increase			Animal manures, fertilizer	Detailed plant growth and simple soil SOM models introduce uncertainty (Riedo *et al.*, 2000)	Riedo *et al.* (2000)
6	DAISY	Plant water uptake, temperature, soil water dependent		Vertical percolation				Animal manures, fertilizer	No N_2O	Grant (1995), Shaffer and Ma (2001)

(*Continued*)

Table 2 (*Continued*)

(b)

ID	Models	Processes, transformations, losses relevant to climate change: Plant: Climate	Plant: Shoot:root	Hydrology	Other	Pollution Swapping (C, N, P)	Mitigation	Farmer adaptations	Limitations	Source of info (see references in full)
7	DAYCENT (daily CENTURY)	Soil temperature, plant temperature, plant water	Allocation to roots increases as precipitation decreases, and a function of time since planting for crops	Vertical percolation		C dynamics		Limited organic waste	Only vertical drainage	Parton *et al.* (1987, 1998, 2001), Shaffer and Ma (2001)
8	ECOSYS	Plant uptake, temperature						Animal manures	Can be too detailed for application with greater calibration requirement	Shaffer and Ma (2001)
9	EUROSEM								Erosion model, vegetation related to obstruction of flow	Morgan *et al.* (1998)
10	EVENFLOW	No climate link with growth or N cycling			Frequency of exceedance of N concentration				Crop processes limited, isolated N cycle	Schoumans and Silgram (2003)
11	GLEAMS	Soil temperature, plant temperature		Vertical percolation				Animal manures	No N_2O	Leonard *et al.* (1987)
12	HURLEY	Yes, very specific, soil moisture, soil temp	Yes, very specific	Some representation	Energy, physiological effects of CO_2 increase				No N_2O	Thornley and Verberne (1989), Arah *et al.* (1997)
13	INCA	Soil moisture, air and soil temperature, plant water		Matrix (slow) and macro- (fast) drainage	Land-use change		Various crops	Manure, fertilizer application	No C cycling or microbes	Whitehead *et al.* (1998), Wade *et al.* (2002)

14	MACRO	Soil temperature, plant water, rainfall, temperature		Multilayer, macro/micro				Limited organic waste	Pesticide model rather than nutrients	Jarvis (1994)
15	MONERIS								Very coarse scale, simplistic	Venohr *et al.* (2005), Schoumans and Silgram (2003)
16	MOTOR (review based on Verberne version, although modifiable)	Indirect reduction factors to rates for drying of soil or temperature effects; fixed weather files	Plant processes not explicitly modeled	Verberne version: water flow not explicitly modeled	Emphasis on microbial effects, isotropic tracers modeled	C and microbial dynamics with N	Different crop types	Manure application	Steep learning curve, no GHG's, no productivity (yield) versus pollution information	Whitmore, 2007, Verberne *et al.* (1990)
17	NGAUGE	Temperature not from observed weather data		Precipitation, not observed weather data			Manure, fertilizer	Animal manures	Isolated N cycling, no carbon or microbes, fixed weather	Brown *et al.* (2005)
18	NOPOLU								Coarse scale	Schoumans and Silgram (2003)
19	OVERSEER	Limited climate variation		Topographic slope and flow with land management					Coarse temporal scale	Ledgard *et al.* (1999), Wheeler *et al.* (2008)
20	PSYCHIC	Monthly long-term statistical means of rain, temperature, sun hours		Drainage, runoff						Davison *et al.* (2008), Stromqvist *et al.* (2008)
21	REALTA								Coarse a scale	Magette, 1998, Schoumans and Silgram (2003)

(*Continued*)

Table 2 (*Continued*)

(b)

ID	Models	Processes, transformations, losses relevant to climate change				Pollution Swapping (C, N, P)	Mitigation	Farmer adaptations	Limitations	Source of info (see references in full)
		Plant								
		Climate	Shoot:root	Hydrology	Other					
22	RZWQM	Plant uptake, soil temperature, plant nutrients	Not considered	Infiltration, drainage			Fertilizer recommendation	Manure applications, growing seasons, animal weight, grazing/ cutting, dairy cow intake	Simple soil hydrological flow	Ma *et al.* (2001), Shibu *et al.* (2006)
23	SIMSDAIRY	Temperature not from observed weather data	Not considered	Precipitation, not observed weather data			Fertilizer recommendation	Animal manures	Isolated N cycling, no carbon or microbes	Del Prado *et al.* (2006)
24	SOIL + SOILN	Plant uptake, temperatures, soil water (derived)	N uptake function of root distribution	Vertical and lateral		C and microbial dynamics with N	Fertilizer recommendation	Manure applications, growing seasons	A good model but SPACSYS has further developed on this model, for example, root component	Eckersten *et al.* (1996), Janssen (1998), Shaffer and Ma (2001)
25	SOMM	Soil temperature, soil moisture			Earthworm decomposition of humic substance		Natural/grazed system/forest biomass		Specialized SOM mineralization and humification derived from microorganisms/ microfauna experiments	Chertov *et al.* (1995)

26	SOURCE AP								Too simple, no soil processes	National Environmental Research Institute (2000), Schoumans and Silgram (2003)
27	SPACSYS	Plant uptake, soil temperature, plant nutrients	1D and 3D comprehensive root system implemented	Infiltration, drainage and lateral	Changes in root architecture, salt dynamics	C and microbial dynamics with N	Fertilizer recommendation	Manure applications, growing seasons, tillage, fertilizer	P component not added yet	Wu *et al.* (2007)
28	MODCOU	Soil water, and temperature		Vertical and lateral			Fertilizer recommendation	Manure applications, growing seasons	No N_2O	Ledoux *et al.* (2002)
29	MAGEC/ SUNDIAL	Plant uptake maximum and minimum temperature, rainfall and ET required	Root:shoot ratio to maximize uptake	Vertical only			Fertilizer recommendation	Manure applications	No N_2O	Bradbury *et al.* (1993), Smith *et al.* (2006)
30	UK-DNDC/ DNDC	Soil temperature, hydrology			Forest and wetland versions	Weakness in hydrology limits leaching versus GHG's	Fertilizer and manure	Different crops, woodland biomass, tillage	Not well developed water module, not detailed partitioning for crop	Brown *et al.* (2002), Li *et al.* (1997, 2010), Shaffer and Ma (2001)

Note: For brevity in table, min/immobiliz, mineralization and immobilization processes.

atmosphere (Cardenas *et al*., 2010; Cooter *et al*., 2010). Good management systems will try to avoid N application immediately preceding heavy precipitation to minimize NH_4^+ loss, so simulating runoff and associated NH_4^+ loss may not rank so high in importance to us as simulating soil water drainage and associated NO_3^- loss. Since N_2O emitted into the atmosphere is 310 times more potent than CO_2 (Cuellar and Webber, 2008), it is logical to also include it as an essential output for soil flux model simulation. Neither NO_3^- loss nor N_2O losses can be completely eliminated from a farming system, but we can determine which land management strategy gives the overall optimal balance between farming and associated N losses and this is why a useful model should include both outputs.

The dynamics of carbon (C) and N is core to the processes affecting leaching and N_2O emission in the majority of published soil N cycle models/modules. New ideas about organic decomposition and nutrient cycling can be implied from results of isotope studies (Amelung *et al*., 2008; Bol *et al*., 2009). For example, it has been shown that some fungi feed only on fresh plant material, little evidence has been found of inert soil C and there is nutrient flow information from the dissipation of bacterially derived C and N through soil food webs (Murray *et al*., 2009). However, many recent ideas have not been formed into a coherent system which has been used in many computer models; simulations are based firmly on the traditional understanding of organic matter dynamics. Carbon and N occur together in all types of organic matter in varying ratios. Organic matter plus applied nutrients are cycled in the soil through various decomposition stages, partially acting as assimilate for the microbial biomass which transforms it (DeBusk *et al*., 2001). Ratios of C:N vary through these stages, and an excess organic matter with lower C:N ratios can result in an excess of N which the microbes will release resulting in N mineralization. High C:N ratios will cause the microbes to immobilize soil mineral N to convert into an organic complex with C. Both immobilization and mineralization can occur, and if the result is net mineralization, excess mineral N in the soil could be at risk to produce leachate through excess water percolation. After mineralization, several things could happen. Under aerobic conditions (dry soil), the nitrifying microbes convert NH_4^+ to NO_3^-, rendering it susceptible to leaching when the soil rewets. NO_3^- diffusing into anaerobic soil layers (wet soil) can also be reduced by denitrifying microbes to N_2O, a potent GHGs. Hence a change in climate, or in land management adapting to the changing climate, will stimulate a change in microbial activity and organic matter turnover (Bond-Lamberty and Thomson, 2010; Lal, 2004), and hence affect leaching and gaseous emission, the two processes being systematically related. Thus, it would be preferable to use a model which includes a sophisticated organic matter turnover simulation.

The detrimental environmental impacts of agriculture can only be minimized if there is more efficient use and recycling of nitrogen and phosphorus (Tilman, 1999).

Manures represent a substantial resource of N and P but have smaller N: P ratios (2–6:1) than most crop requirements (7–11:1), leading to soil P enrichment over time. It is necessary from an economic yield aspect to maintain a high plant P-use efficiency over time, and to do so, it is necessary to build up the soil P to a critical level, at which there is a high percentage recovery of phosphorus from fertilizer in crop harvest offtake. In developed countries, where soil P is in excess, farmers attempt to strike an economically viable balance between maintaining a soil at a critical level while preventing excessive phosphorus levels. European agriculture is currently operating on an annual P surplus, which can have a major impact on water quality (Dils *et al.*, 2001). It will therefore be important to include P cycling in an integrated multinutrient model, but this could limit the choice of a more advanced model of C and N dynamics, in which case it would be better if either P were simulated by a separate model or, in the longer term, a new holistic N, C, and P model were developed.

We have included in our chapter, models that simulate a particular nutrient cycle in isolation such as the N cycle in NGAUGE, or focus on a particular process, for example, erosion in EUROSEM. These were useful to review because there is the possibility of using them in a framework with other models, for example, an N model related to soil moisture via a water flow model being added, or a stream-routing model with an agricultural management model added. Sometimes certain models are particularly strong in one feature, shown by that process being simulated in more detail than others. We try to show the diverse methods by which models simulate processes in the following sections and focus on what is included or missing from a model for our study. The next section breaks modeling details down into criteria, discussing merits and limitations of the listed models.

2.2. Model issues with regards to climate change impact

2.2.1. General background

The rates of most biological processes are sensitive to the factors of temperature and water availability being related to enzyme activity. Considering future climate effects (essential now in most studies of environmental processes), we need to know by how much climate changes from a historical baseline. Climate scenarios from general circulation models (GCMs) provide us with this information. In order to assess the impacts of climate change on diffuse pollution, and the effects of mitigation management practices and adaptation on diffuse water pollution, models need to be able to directly or indirectly use climate data, and preferably use climate scenarios. This would mean a direct use of observed climate parameters and

future climate scenarios on a daily basis. Alternately, an indirect use of climate data, such as a modification of a fixed climate, could also be considered.

Climate parameters are driving variables for energy transformation, water balance, plant growth, and nutrient cycles in agricultural production systems. Therefore, the parameters of temperature and precipitation as a minimum requirement should be included in a model. Daily maximum and minimum air temperature should be integral to a model for determining climate information and crop processes. Knowing the minimum temperature allows an approximate assessment of whether precipitation will be in the form of snow which can increase soil surface water retention time and can delay flow. Minimum temperature also influences vernalization for annual over-winter plants and determines the date of flag leaf appearance for cereal crops (Slafer and Rawson, 1995). Most soil–crop–weather models require a time function for crop development which may be a calendar time or heat unit accumulation. Robertson (1968) introduced the concept of biometeorological time, involving photoperiod, maximum and minimum temperature, for calculating the rate of development of different crop stages. Photoperiod is a preferred climate parameter relating to crop development but it can be calculated using Julian day and latitude. Likewise, wind and humidity would be preferred parameters to allow a calculation of evapotranspiration which will affect crop growth and development rate and the soil water balance.

Results have shown from two decades of free-air CO_2 enrichment (FACE) experiments that elevated CO_2 stimulates photosynthetic carbon gain but increase in crop yield is smaller than expected (Leakey *et al.*, 2009). Plant responses to CO_2 vary and underlying mechanisms are not clearly understood, hence it is not considered an essential simulation to include in a model. However, the PASIM and HURLEY models and SPACSYS have the option to include a range of atmospheric CO_2 concentrations.

2.2.2. Observed or simulated climate files

ANIMO does not use direct weather data, instead it uses output from earlier run weather-driven simulations with a separate soil water model, operating at the same timestep as the soil water simulations, daily or weekly. NGAUGE and $SIMS_{DAIRY}$ have a static climate file derived from historical climate statistics instead of observed climate. GLEAMS can take climate data from observed or simulated sources and it operates on a daily timestep, using observed weather data to drive the hydrology, erosion, and temperature submodels. An optional climate generator can be used within GLEAMS for daily rainfall, temperature, and radiation data. Otherwise, most complex models with a shorter timestep use observed climate data, such as APSIM, RZWQM, DAYCENT, MAGEC, and SPACSYS, requiring daily timestep weather data to drive the

hydrology, energy, and nutrient submodels. MACRO operates with observed weather data on a daily, hourly, or shorter timestep.

2.2.3. Precipitation

The fixed climate files of NGAUGE and its farmscale extension $SIMS_{DAIRY}$ take the 30-year mean monthly precipitation for locations around the UK, and there is a choice of one of six rainfall values. Precipitation indirectly impacts on the submodels of denitrification, mineralization, and plant uptake. Each precipitation file can be modified by a fixed amount to give five classes representing a very wet to very dry month. It is recognized that the period since precipitation is a major factor in determining denitrification rate (Jarvis *et al.*, 1991), so the temporal and spatial scales are a limiting factor. It is the monthly and longer timestep models which sometimes use a derivation from climate archives like NGAUGE and $SIMS_{DAIRY}$, most use weekly rainfall. ANIMO takes daily precipitation information from its separate hydrological model. MAGEC, RZWQM, DAYCENT, SPACSYS, APSIM use daily precipitation. As regards climate change, any annually scaled models for precipitation are immediately limited in terms of adaptation, as they cannot use climate data seasonally, that is, drier summers or wetter winters.

2.2.4. Temperature

Soil nutrient–microbe dynamics are temperature dependent, and demonstrating a typical modeled C and N cycle response with respect to air temperature change, a sensitivity test was conducted on MAGEC (Smith *et al.*, 2006). When temperature was increased, amounts of decomposable and resistant organic pools were reduced. Mineralization and denitrification were significantly increased reflecting increased microbial activity. Nitrate and ammonium in the soil, along with leaching, were reduced, possibly with increased microbial N requirement (Smith *et al.*, 2006). Many of the models reviewed such as MACRO, GLEAMS, DAYCENT, and ANIMO require daily air temperature to calculate daily soil temperature and thermal conductivity, which affect the chemical and biological processes (Lewis and McGechan, 2002). The dependence of N processes is based on air rather than soil temperature in the SUNDIAL model (Smith *et al.*, 2004), the model inputs average weekly air temperature. SPACSYS requiring daily maximum and minimum air temperature has a specific soil thermodynamics portion of the model, with optional extra components such as ice water infiltration and snow dynamics. In some models, for example, SOIL and SOILN, heat modules link soil water and heat with freezing and thawing of soil water (Bergstrom *et al.*, 1991; Lewis and McGechan, 1999). In other models, the temperature comes from a derivation of archived climate data. The fixed climate files of NGAUGE and $SIMS_{DAIRY}$ take the 30-year mean monthly temperature for locations around Britain, and there is a choice of

one of six temperature zones. Weather impacts on the submodels of denitrification, mineralization, and plant uptake. Each temperature file can be modified by a fixed amount to give five classes representing a very warm to very cold month (Brown *et al.*, 2005; Del Prado *et al.*, 2010).

2.3. Consideration of the water cycle

2.3.1. General background

Soil water modules are often used to link climate into other soil processes via evapotranspiration and precipitation. Chemical and physical processes in nutrient cycling such as a portion of N mineralization and immobilization are modified by soil moisture and also by water flow. Water is also important as a carrier for the mobility of nutrients into and out of soil layers. Most models have some form of water balance, shown in Table 2b. Since we are reviewing models to determine the effect of climate change on diffuse pollution, a simulation of water balance and availability would be useful. Results have shown NH_4^+ to be lost predominantly by runoff, while NO_3^- is lost into streams by percolation of water through soil (Eunice Lord, ADAS, personal communication, 2010; Fey *et al.*, 2010; Lu *et al.*, 2009). Hence, runoff and leaching are both important processes depending on the expectation of simulation output.

2.3.2. Water balance

Soil water models generally require hydraulic conductivity and water response functions for various soil layers (DeJong and Bootsma, 1996) to determine throughflow or a deficit. Whereas ANIMO uses a separate soil water module, NGAUGE and $SIMS_{DAIRY}$ have no soil water processes simulated within the models, but soil moisture deficit is read as an input with the weather files. The percentage water-filled pore space in these two models (related to soil moisture deficit) modifies N processes and is related to monthly denitrification using a relationship based on experiments (Scholefield *et al.*, 1997).

GLEAMS, an update of the CREAMS model for nutrient and pesticide flow and RZWQM (Shibu *et al.*, 2006), determines surface runoff by employing the surface runoff curve number technique with evapotranspiration and soil-routing simulations. The Soil Conservation Service Curve Number (SCS-CN; Tramblay *et al.*, 2010; US Department of Agriculture Soil Conservation Service, 1972) is a method to determine soil water runoff, or overland flow, depending on antecedent moisture conditions. The method is based on two hypotheses: that the ratio of direct runoff to potential maximum runoff is equal to the ratio of direct soil infiltration to maximum potential soil retention and that initial abstraction, or temporary surface storage, for example, puddles, is a fraction, commonly 20%, of the potential maximum soil retention. SCS-CN has been widely used for

flooding because it uses a minimal number of parameters compared to other methods. GLEAMS also uses two optional calculations of evapotranspiration depending on climate parameters available, which is a very practical step, considering data sources vary or have missing data. GLEAMS can also account for irrigation.

Models deal with soil moisture throughout the soil layers differently depending on their soil water complexity: GLEAMS uses five soil layers; RZWQM and DAYCENT (the daily scaled CENTURY model) use 10 layers. GLEAMS can relate the water balance to wetland, subsurface drainage, and tillage systems. SPACSYS can have unlimited soil layers, it stores water in surface, matrix pool, or canopy pools, extra water from a groundwater source can occur, and the water in the soil matrix can be redistributed since it uses SOIL's numerical solution to the Richards equation (Janssen, 1998). This a common feature in other models such as DAISY which also employs Richard's equation requiring water release characteristics and hydraulic conductivity. PASIM can also have an unlimited amount of soil layers and, like SPACSYS, employs Darcy law so that water fluxes between soil layers relating to percolation, capillary rise, and drainage depend on soil water content, matric potential, and hydraulic conductivity. UK-DNDC and the 2002 version of DNDC employ a "tipping bucket" method of vertical soil drainage through layers, that is, when field capacity is reached, 50% of the water over this threshold moves into the soil layer below. In addition, gravitational redistribution and matric redistribution of soil water (Ritchie, 1998) are then employed.

2.3.3. Runoff, water movement, and drainage

The hydrological component of GLEAMS, EVENFLOW, and RZWQM simulate runoff using an adaptation of the SCS curve number method (Tramblay *et al.*, 2010; US Department of Agriculture Soil Conservation Service, 1972). The downward movement of water is simply based on the excess of field capacity for many models such as GLEAMS, RZWQM, SUNDIAL, and MAGEC. Other models such as DAISY and SPACSYS base their soil water on the Richards equation (Richards, 1931), relating water flow to hydraulic conductivity and water tension. DAYCENT has multiple soil layers for water flow. MACRO, a model particularly strong in water flow through soil, has its own module for multiple soil layers and water movement in macro- and soil matrix pores.

GLEAMS and DAYCENT only consider vertical flow, not lateral flow under the soil surface. MACRO and SPACSYS consider flow to groundwater and subsurface lateral flow to field drains. GLEAMS therefore simulates the vertical transport of nutrients and pesticides down through root layers, and its surface flow detaches and deposits sediments providing transport for the full description of C, N, and P cycles contained within GLEAMS. Contrasting with detailed nutrient transport processes,

NGAUGE and $SIMS_{DAIRY}$ simply relate water-filled pore space to a leaching component, but their emphasis is the N cycle.

SPACSYS is a complex, process-based, integrated agroecosystem model. It has a daily timestep and operates at the field scale. Driven by weather, it has a thorough water flow module for field drainage and vertical flow plus groundwater flow. Water flow interacts with plant growth, separated into consideration of roots and above ground processes. Ammonium and NO_3^- are included in vertical drainage and in groundwater flow; surface runoff loss of organic matter is also an output in water flows.

MACRO has been recommended for use as a tool to study leaching (Mantovi *et al.*, 2006). Nitrate accumulation in surface soil during warm periods was shown to be susceptible to fast drainage related to shrinking/swelling properties of clay minerals. The model results confirmed the observed role of macroporosity in accelerating the throughflow of soluble compounds. MACRO has separate simulations of contaminant flow in soil matrix pores (micropores) and macropores, as well as contaminant movements between the two domains. MACRO simulates water movements vertically through the profile including deep groundwater and horizontally to field (tile) drains. The hydrological routines in MACRO are similar to many other soil water models, with the soil water tension and hydraulic conductivity relationships enabling the Richards' equation to be solved (Richards, 1931). MACRO differs from other models in its treatment of larger soil macropores when capillary forces are very low, so water movements can be assumed to be driven by gravitational forces alone (McGechan *et al.*, 2008).

APSIM has been used to explore components of the water balance for a range of farming systems. APSIM was used to explore the impact of climate on water balance, with all other factors held constant, including the soil type. The impact of climate on water balance was said to identify the relative magnitude of transpiration, soil evaporation, runoff, and drainage and to explore temporal variability in these terms for selected locations over the 1957–1998 climate record (Keating *et al.*, 2001). Evidently, then APSIM appears suitable to investigate the effect of climate change scenarios on soil hydrology.

We can group models into their resultant output by referring to Table 2b. ANIMO, APSIM, PASIM, DAISY, DAYCENT, INCA, MACRO, RZWQM, SOILN, SPACSYS, MODCOU, and MAGEC produce vertical drainage. ANIMO, SPACSYS, and SOILN produce lateral flow to field drains. The documents that we have reviewed for ECOSYS, EUROSEM, MACRO, MOTOR, NOPOLU, SOMM, and SOURCE AP do not specify that they output leached nitrate.

2.3.4. Catchment flow

A few models such as EVENFLOW, MONERIS, NOPOLU, SOURCEAP, REALTA, and PSYCHIC are strong catchment models, considering stream pollution (Table 2a). The HSPF model is packaged in open GIS

form as BASINS. Using web-based data for a geographic location is a strong tool for multiple nonpoint source data considering surface flow drainage over catchments to one or multiple rivers, but it is not an agricultural tool. BASINS would however have potential if linked with a model simulating agricultural land management effects on nutrient cycling. It can consider fecal indicator organisms, P and sediment transport, and can link with inputs of biota in watersheds, for example, indices such as biodiversity of invertebrates representing the fitness of aquatic communities. BASINS can utilize online climate scenarios. However, without agricultural management, it is limited for our application, and further since it is an American model, having a full complement of data for other countries in its GIS database is doubtful. When a model is using online data, this can be useful to access data availability, but there is no control over the quality of the data, and questions arise of flexibility and specifically of the ability to use one's own observed data.

EUROSEM is an erosion impact model, useful therefore for determining sediment transport and relating to nutrient loss. Like HSPF/BASINS, it focuses on strong water flow modeling to catchment scale, but instead of stream loading, it focuses on erosion of the gulleys and channels. It is not an agricultural model and lacks land management, its consideration of vegetation is related to interception and infiltration, but as with BASINS, such a model would be useful linked to a land and nutrient management model.

INCA also accounts for water flow to a catchment. Inputs required are climate, initial water flow and N loading, land management, fertilizer timing and application, crop type, and sewage flow rate. Key processes are mineralization, immobilization, denitrification, nitrification, plant uptake of nitrate, and ammonium; the concentration of these is dependent on the water cycle. The process equations are solved in a manner ensuring that no one process takes precedence over the others. Parameter sets are derived through calibration, that is, model parameters being adjusted a little at a time until the difference in observed and simulated data is acceptable. Hydrological calibration is key to this because it controls N stored and transferred. Soil, air temperature, and hydrological processes incorporate features suitable for climate change applications. INCA has really been designed for studying river system functioning, nevertheless, it does include all agricultural soil N processes and land use and land management.

2.4. Capability for nutrients and carbon cycling

2.4.1. C and N coupling

Soil C and N dynamics affect crop and soil quality, as well as the resulting pollution from agriculture. Through their greenhouse effects, they have an influence on the stability of the climate. In recent years, it is this global environmental importance that has resulted in a focus on this subject, while

at the same time, new biogeochemical tools have been developed which can improve understanding of these cycles, for example, isotope tracing and remote measurement techniques (Amelung *et al.*, 2008; Boegh *et al.*, 2004; Bol *et al.*, 2009; Gilmanov *et al.*, 2010; Rubino *et al.*, 2010). Meanwhile faster computing has enabled improvements in modeling, especially at field or microscale, to include more mathematical complexity in the simulation of processes, which has enabled the improvement of models of C and N dynamics (Lu *et al.*, 2006; Ptashnyk *et al.*, 2010).

There are knowledge gaps in the fine details of C and N cycle processes, so they are commonly modeled using pools of common components within a cycle and, from experimental results, transformation rates are determined between the pools. Some models simulated the N cycle without linkage to the dynamics of the C cycle, for example, NGAUGE. However, C and N dynamics are intricately linked via microbial growth and turnover. Modeling trends have moved away from isolated nutrient cycles (Bergstrom *et al.*, 1991; Brown *et al.*, 2005; Chertov *et al.*, 1995) toward integrated simulations of multinutrient cycles, also incorporating crop, atmosphere, microbial biomass, soil water, and other components (Grant, 1997; Groenendijk and Kroes, 1999; Wu *et al.*, 2007). Some models have developed separately from the original model. For example, UK-DNDC and DNDC (Li *et al.*, 1997) have similar functions, but UK-DNDC (Brown *et al.*, 2005) was modified for use in the UK and both have been updated separately since.

2.4.2. Mineralization/immobilization

Heterotrophic soil microorganisms, primarily fungi and bacteria, use C from decomposition in a specific proportion with N (C:N ratio of ca. 6) which they obtain from mineralization of organic N, soil NO_3^-, or NH_4^+. If microbial organisms are supplied with C rich and N poor residues (generally anything with C:N ratio over 30) such as wheat straw, this will result in immobilization of N in the biomass, leaving little N available to a growing crop. N is released with microbial turnover, or when microbes are consumed by higher trophic levels which excrete excess N, resulting in N mineralization. Conversely, decomposing organic materials with lower C:N ratios can result in an excess of N and net soil mineralization (Chadwick *et al.*, 2000; Shaffer and Ma, 2001). Simulations adopt a mixture of methods to represent mineralization and immobilization.

Models which integrate simulation of the C and N cycles commonly capitalize on the C:N ratio as the key link between the two nutrient cycles and a way of determining net N immobilization and mineralization (DNDC, SPACSYS, SOILN, DAYCENT), a C:N value above a threshold value signifies immobilization (high organic C residues after harvest and ploughing), and a value under the threshold signifies net N mineralization. Meanwhile, the rates of the processes plus microbial growth and decay are influenced by temperature and soil moisture (Melillo *et al.*, 1989).

In RZWQM, mineralization and immobilization are determined by the decay of organic pools and growth of microbes. Organic pools decay according to a first-order equation and the rate coefficients are modified for temperature and moisture effects. It is assumed that a fraction of organic C decayed becomes part of the microbial biomass, and the N assimilated into microbes is calculated via the C:N ratio. RZWQM separates soil functions by different microbial groups, for example, it is the aerobic heterotrophs which obtain their energy and growth via organic pool decay. In GLEAMS, organic pools also decay according to first-order reactions.

NGAUGE and $SIMS_{DAIRY}$ calculate N mineralization empirically. These models do not account for organic C, so do not link C:N ratios to organic matter cycling. Annual preexisting mineralization is calculated from previous land use, herbage production, dung, and applied manures, based on experimental results and modified by sward age, soil texture, and drainage. The values are partitioned between 12 months. Mineralization is modified by 30-year means of temperature and soil moisture from specific locations in the UK. Mineralization is added from the current year's residues empirically derived and based on monthly plant N content. A key feature of this process is that for each monthly timestep the model iterates through the N cycle, until the resulting value returned from the previous step in the cycle for mineralization is within a threshold difference.

Not all models have to have a detailed description of N processes. MONERIS considers soil N simplistically, mineralization and immobilization are ignored, and the net N surplus (input minus harvest offtake) is assumed to be released as dissolved inorganic nitrogen. In EVENFLOW, there is no explicit representation of the N cycle, being based on empirical relationships between cropping and grazing regimes and nutrient output instead.

Among the catchment models, SOURCE AP, REALTA, and NOPOLU do not consider soil processes but can nonetheless serve as "broad brush" tools to assess pollutant loads at catchment level (Schoumans and Silgram, 2003). For all these models, soil processes are lumped and implicitly derived from measured monitoring data.

2.4.3. Denitrification/nitrification and nitrous oxide emission

Representations for nitrification/denitrification vary among models, often in accordance with the complexity of the whole model. In SOILN, ANIMO, and DAISY, nitrification is determined by a nitrification rate, NH_4^+ content, and environmental modifiers of the rate (Hansen *et al.*, 1991; Ma and Shaffer, 2001; McGechan and Wu, 2001).

NGAUGE and $SIMS_{DAIRY}$ use this approach, too. Their source of ammonium is pools of ammonium mineralized from organic matter, including excreta, NH_4^+ from fertilizer, and urine from slurry application.

Nitrification in NGAUGE and $SIMS_{DAIRY}$ is a zero-order reaction, hence independent of substrate concentration but with temperature and moisture modifying the rate. Processes producing NO and N_2O have a representative value to produce a maximum amount, a modifier accounting for moisture and the amount of ammonium nitrified (Brown *et al.*, 2005). Denitrification is simulated as a function of the amount of inorganic N modified by temperature and moisture. Considerable temporal and spatial variations in denitrification rate occur in the field, and during a dry month, a sudden downpour increases the denitrification rate, so a limiting factor of a monthly model is that it obscures temporal variation. Production of N_2O and N_2 is determined by the denitrification rate modified by the minimum of three factors; water-filled pore space in soil (related to moisture), mineralization rate, and the amount of mineralized N.

In APSIM, nitrified N_2O is proportional to the nitrification rate. The simulation of the N_2:N_2O ratio from denitrification is related to the amount of nitrate to heterotrophic CO_2 respiration (Thorburn *et al.*, 2010).

The complex ECOSYS model links the net mineralization to the nitrification process. Each microbe functional type in each substrate–microbe complex seeks a consistency of its C:N ratio during growth by mineralizing or by immobilizing ammonium. These reactions control soil mineral N concentrations which in turn drive nitrification and denitrification reactions in the model (Grant *et al.*, 2006). ECOSYS is a model based on physiochemical transformations, such as oxidizing reducing equations and energy transformations, and considers eight types of microbe separately.

RZWQM considers functional groups of microbes separately, autotrophs obtain their energy from nitrification, and a fraction of NH_4^+ is assimilated, whereas facultative heterotrophs grow via denitrification and take a fraction of denitrified NO_3^-. RZWQM calculates nitrification as a zero-order rate modified by temperature, pH, autotroph biomass, and oxygen content. Unlike most models, RZWQM can account for nitrification inhibitor application. Denitrification is determined by a first-order rate coefficient modified by soil C, lack of oxygen, temperature, pH, and denitrifier biomass.

DAYCENT calculates nitrification to be proportional to mineral N turnover, and its N_2O production to be related to turnover rate and excess ammonium in the soil. N gas fluxes from nitrification and denitrification are driven by soil NH_4^+ and NO_3^- concentrations, water content, temperature, soil texture, and labile C availability. DAYCENT's simulation of combined N_2O plus N_2 gas flux from denitrification is limited by the minimum value of three factors: (1) maximum N gas flux for a given soil respiration rate, (2) for NO_3^- content, and (3) the soil moisture effect on denitrification.

DNDC's denitrification module tracks microbial dynamics and availability of substrate (NO_3^-) and modifies the rate reaction on the substrate by

moisture and temperature (Zhang *et al.*, 2002). ANIMO links denitrification to the amount of decomposable organic matter; SOILN connects denitrification to the amount of NO_3^-; and DAISY relates denitrification to the amount of NO_3^-, organic decomposition, and emission of CO_2 (Hansen *et al.*, 1991; McGechan and Wu, 2001).

Denitrification in the OVERSEER model is based on IPCC methodology where the amount of each type of N input into the system (excreta, fertilizer, effluent) is multiplied by the emissions factor for that type of N source. Excreta from livestock is partitioned into urine and dung, and further partitioned into paddocks, lanes, dairy, or housing. Dairy and housing contribute to the effluent system.

The variety of different empirical methods reflects the unknown nature of the processes of nitrification and denitrification, which are so complex and vary in time and space with different species of microbes affected by varying environmental factors in the soil.

Referring to Table 2a, the models which specifically output N_2O are PASIM, DAYCENT, ECOSYS, NGAUGE, $SIMS_{DAIRY}$, RZWQM, SPACSYS, and UK-DNDC.

2.4.4. Organic matter decomposition, carbon and nitrogen dynamics

Most models (e.g., MOTOR, UK-DNDC, DAYCENT, RZWQM) link the C and N cycles by the ratio in which they are found in their organic matter component, thus knowing how much C gives the amount of N and vice versa. Simulated C and N dynamics commonly comprise algorithms for the decomposition of organic matter combined with plant uptake; mineralization/immobilization; and, if included denitrification and nitrification, input of plant litter, manure, and root exudates.

The core algorithms of C and N dynamics are the C decomposition of organic matter pools. These vary across models but are generally split into fast decomposition pools with a higher C:N ratio such as fresh litter, and slow more stable decomposition such as humus with a lower C:N ratio. This concept can be seen in GLEAMS, MAGEC, RZWQM, and SPACSYS. The nutrient model of GLEAMS has an organic matter and microbial pool dynamically linked to the N and P cycles. GLEAMS incorporates crop residue and active and stable organic matter pools. MAGEC links decomposition and C:N ratio to soil type. RZWQM has a specific microbial biomass pool and separates the microbes into aerobic heterotrophs, autotrophs, and facultative heterotrophs. In SPACSYS, organic matter pools have specific decomposition rates further modified by soil water and temperature and the C:N ratio. The C:N ratio in the microbial biomass has a feedback effect on mineralization and immobilization.

SPACSYS has four organic matter pools: (1) fresh organic material, (2) humus, (3) dissolved organic matter, and (4) microbial biomass. Part of the

organic matter dynamics also includes dissolved organic carbon (DOC) from residues lost from the surface of the soil in runoff, and DOC lost from within soil by leaching.

PASIM has C fluxes moving between an animal submodel, a plant submodel, and a soil submodel. Considering this represents grazing from grass to animal, urine/feces from animal to soil, and root exudation from plant to soil, this is a framework common to other models.

CENTURY/DAYCENT separates plant residues into structural lignin and structural cellulose pools and a metabolic pool based on the lignin:N ratio. Metabolic and cellulose pools are more active, and lignin the stable pool. DAYCENT decomposition of litter and soil organic matter and nutrient mineralization are functions of substrate availability, substrate quality (lignin %, C:N ratio), and water/temperature stress (Parton *et al.*, 2001). The final residual organic fraction which cannot be further broken down (condensed tannins, phenolics, waxy alkyl compounds, and lignins) is referred to as the acid unhydrolyzable residue (AUR). The CENTURY model, when applied to leaf litter only, has 5C pools: structural, metabolic, microbial (or active), slow, and passive. The undecomposed litter is divided into the structural and metabolic pools, as determined by the AUR/nitrogen ratio, the higher this ratio, the more of the organic matter in the litter is considered to be structural. Carbon from the structural and metabolic pools is partitioned into CO_2 losses and transfers to the active and slow pools, and further CO_2 losses with transfers to the passive pool. Pool-centered decomposition rates are calculated empirically by reducing a maximum decomposition rate by a multiplicative function that depends on mean July temperatures and annual precipitation rates. The N pools and processes are considered to have same structure as the C pools and processes, with prescribed C:N ratios by pool type. N rates entering or leaving the pools are adjusted such that the C:N ratio of each pool remains fixed, except for the C:N ratio of the metabolic pool which is allowed to vary. External N inputs are via atmospheric deposition and fertilizer applications or N_2 fixation (Del Grosso *et al.*, 2009).

In ECOSYS, microbial biomass is an active agent of organic matter transformation in the model. Soil organic matter is divided into four substrate–microbe complexes: plant residue, animal manure, particulate (active), and nonparticulate (passive) organic matter in five different states: solid, solubilized, adsorbed, microbial, and microbial residue. Each organic state in each complex is further divided into carbohydrate, cellulose, and lignin with varying rates of relative decomposition. Microbial communities are further grouped into obligate aerobic and anaerobic, facultative anaerobic, and methanogens (Grant, 1997). Rates of decomposition of each substrate–microbe complex depend on the substrate–microbe density relationships, temperature, and water content. Residue decomposition products depend on soil clay content.

SOMM considers organic decomposition and the N cycle separately (Zhang *et al.*, 2008) and includes mineralization and humification by microbes and soil fauna with separate soil microfauna and mesofauna pools. Limited in its view, SOMM could be useful seen as an addition to models which lack this aspect such as NGAUGE and $SIMS_{DAIRY}$. However, in comparison with other models such as CENTURY, it was found to require far more temperature and moisture sensitivity coefficients (Zhang *et al.*, 2008), since each coefficient empirically derives from independent process studies, for each of the mass and N turnover processes. Despite its greater parameter requirement, SOMM simulations tested against experimental measurements were not found to give as high a quality of fit between calculated and observed values for mass remaining and N concentrations over time as CENTURY.

MOTOR is primarily concerned with the flow of C linked to N via the C:N ratio's of different matter. The model deduces the fraction of each source pool that within a daily timestep becomes a particular product in another pool. The fractions are multiplied by the rate term and the amount of C in the source pool can be modified by the efficiency of the process (Verberne *et al.*, 1990). MOTOR is based on a body of work including the Verberne organic matter turnover model (Verberne *et al.*, 1990). The system tries to accommodate the change in C:N ratio during nutrient flows. Gross mineralization of N determines its supply and immobilization its demand. The supply and demand are compared, and if out of balance, there are several strategies used to rebalance the N flow. Decomposition kinetics is modified repeatedly until the supply matches demand. One strategy is to include a partitioning factor, putting emphasis on a greater transformation of a pool to a specific product for which there is a high demand, out of a number of potential products. Another strategy is to reduce the decomposition rate of fresh residue pools (manure and litter). The values of C:N are variable in a pool, although it is stated that how much these latter two strategies reflect real life is unclear. These strategies increase N supply, conversely C retention time in soil can be reduced to reduce excess N. Production of microbial biomass from the residue pool and its decomposition will create a need and an excess of N, respectively. Hence, the microbial turnover is modeled integrally with the nutrient flows. The reaction rates are modified by temperature and soil moisture decreasing from an optimum value as soil dries, although the model has no explicit water simulation.

DNDC's decomposition module quantifies the organic C gain from crop litter (roots and aboveground residue) and/or manure incorporation, as well as the C loss through decomposition. DNDC partitions litter into three soil litter pools, very labile litter, labile litter, and resistant litter, based on the C:N ratio of the bulk litter. There is a specific decomposition rate for each litter pool, modified by temperature, moisture, and N availability in

the soil profile. During the decomposition of litter, part of the litter C is consumed as the energy source by the soil microbes and becomes CO_2, and part of the litter C is turned into microbial biomass. After death, microbial remains will become humus to undergo further decomposition.

2.4.5. Root/shoot partitioning and uptake

Plant N uptake relates to plant growth, root distribution, and integral with this is partitioning to different parts of the plant. DAYCENT and PASIM deal with biomass growth separately for roots and shoots modified by temperature and moisture, and SPACSYS includes root growth in detail apart from the rest of the plant, roots getting priority for assimilate. A component of SPACSYS develops the root architecture, which will have further effects on nutrient uptake. Under substrate shortage, root growth is restricted which modifies the proportion of assimilate translocated to different parts of the plant. SPACSYS also contains a mycorrhizal pool since fungi often attaches to the root system. DAYCENT plant production is a function of genetic potential, phenology, nutrient availability, water/temperature stress, and solar radiation. Net primary production is allocated to plant components (e.g., roots vs. shoots) based on vegetation type, phenology, and water/nutrient stress. Nutrient concentrations of plant components vary within specified limits, depending on vegetation type, and nutrient availability relative to plant demand (Del Grosso *et al.*, 2009).

DNDC root growth is also determined by partitioning of assimilate from crop growth processes, and then rooting processes include the increase of root front depth, distribution of root length density, and biomass. Root depth is limited to a maximum. Daily variation of root density depends on new growth and senescence. Root depth, density, and biomass distributions will affect the capacity to uptake N. SPACSYS has a detailed option to investigate the three-dimensional architecture of roots. This root simulation is related to soil temperature and strength, and water nutrient concentration for growth, and assimilate to determine root elongation and volume expansion. The previous root direction, geotropism and mechanical resistance affect the orientation of a root and root branching is simulated. A simpler option for root growth simulation in SPACSYS considers root growth based, like DNDC, on rooting depth, vertical distribution of root length density, and root biomass.

N uptake in models is usually simulated from plant demand from a crop growth module or from studies using an empirical curve. Some models, for example, DAYCENT, SPACSYS, and RZWQM, have plant growth modules to estimate demand of the inorganic N at different phenological stages. ANIMO bases crop uptake of nutrients on a balance between crop demand and soil supply, and adjusts crop growth rate if the soil supply is limiting. The GLEAMS model assumes uptake of total N. Plant nitrogen is returned to the soil via crop residues and roots. Allocation of assimilate to

roots increases as precipitation decreases; this potentially could be of use in simulating adaptations to climate change.

2.4.6. Phosphorus

ANIMO, GLEAMS, DAYCENT, and MACRO incorporate the P cycle. The models contain the transport of soluble and particulate P, the application of manure and fertilizer and the mineralization/immobilization of organic/inorganic matter. MACRO considers micro- and macroflow containing P and has the capability to simulate the movement through the soil of P bound to particulate material. ANIMO also considers preferential macropore flow. It considers P sorption onto and diffusion within soil particles, described by a combination of instantaneous and time-dependent sorption and chemical precipitation of phosphates, and overland flow of dissolved organic phosphorous, inorganic phosphate, and particulate phosphate with water flow to adjacent fields (runoff and erosion). Erosion and sediment yield from fields is estimated in GLEAMS via soil particle detachment and the subsequent transportation of this sediment. Particle detachment is assumed to be a function of soil properties, management, and rainfall and runoff characteristics.

When runoff occurs, the sediment load is assumed to be limited by the transport capacity; deposition takes place with usually the coarse and dense particles deposited first. DAYCENT considers surface losses from the labile inorganic and active organic P pools. The model also considers soil erosion effects in addition to surface runoff losses.

With respect to P, MONERIS has no sorption and desorption mechanisms, just an overall equation used to describe the relationship between P content of the soil and the P concentration in soil solution (Schoumans and Silgram, 2003). The catchment models focusing on streamloading, REALTA, MONERIS, NOPOLU, and SOURCE AP all consider total P load from land to water, but no detailed soil processes concerning P cycling.

A complete consideration of P in soil should consider transport of both soluble and particulate P, and of both inorganic and organic P, by surface runoff, through the soil to field drains, and vertically through the soil down to deep groundwater. In addition, it should consider the transformations from one form of P to another following applications of both mineral fertilizer and manure (Lewis and McGechan, 2002). Most models considered here seem to be missing one or more of these processes. GLEAMS considers everything except transport to field drains. DAYCENT also only considers vertical transport. ANIMO has the most comprehensive inclusion of manure and slurry, and includes a rigorous description of soluble forms of phosphorus, but lacks consideration of particulate transport. MACRO has the most comprehensive inclusion of through soil transport processes and particulate transport but not surface runoff and currently has only simplistic

representation of P transformations. A comprehensive nutrient model focused on P would be a combination of these four with a full representation of the C:N:P cycle as described by GLEAMS, with manure and slurry components as described by ANIMO, and plant residue decay equations taken from the DAYCENT model. Finally, the overland flow and erosion losses could be represented by components from the GLEAMS model (Lewis and McGechan, 2002).

PSYCHIC accounts for the mobilization and delivery of P and suspended sediment (SS) using empirical data. It includes transport of soluble and particulate P, and inorganic and organic P, by surface runoff, through the soil to field drains and vertically through the soil down to deep groundwater. The model determines the fraction of mobilized phosphorus and sediment delivered down rivers based on the connectivity of drains and watercourses, with preferred particle size for each pathway of diffuse pollution. Over predictions have been reported (Stromqvist *et al.*, 2008) although this seems the most comprehensive P model in our chapter.

2.5. Land management

2.5.1. General modeling issues with respect to land management

This section reviews which models have the ability to simulate agricultural management. It may be the capability to simulate different types of crops and their period of ground cover, or breeds of livestock and timing of grazing, or the timing and application of fertilizer, or a physical alteration of the soil such as tillage. Viewed in light of climate change, these are parameters a farmer can choose to adapt. The most likely mitigation measures we feel would be recommended are listed by (Cuttle *et al.*, 2007).

Any change in either the natural conditions or the farming management can simultaneously alter several soil environmental factors including temperature, moisture, pH, and substrate concentration gradients. This can affect a series of biogeochemical reactions such as physical movement, oxidation and reduction, dissolution, adsorption, assimilation which finally determine CO_2 and N_2O emissions from the modeled ecosystems (Zhang *et al.*, 2002).

For example in SPACSYS, if ploughing is opted for as part of the simulation, all remaining living leaves and stems, roots down to ploughing depth, and all above ground residues are evenly included in the litter pool for that depth. The roots below the ploughing depth are incorporated in the corresponding litter pools (Wu *et al.*, 2007). This has a huge impact on the organic matter cycling via different C:N ratios, soil aeration, and altering active biomass functional types, that is, nitrifiers or denitrifiers.

Considering how farmers may adapt to climate change or what mitigation policies may be made, the most likely seem to be connected to field management strategy, crop types, and the length of time that the ground is covered. Cover crops can reduce NO_3^- loss if well established, using the cover with

crop rotations and accurate timing to reduce leaching (Shepherd *et al*., 1993). The ability to schedule land management events daily is one the most important benefits of a model with a shorter timestep (Del Grosso *et al*., 2009).

As will be seen in Section 2.5, no one model accounts for every agricultural management. Model applications can be divided into those biased toward livestock farming and those biased toward arable. Choice of model for management effects depends on the application required; a mix of use for land-use change may require use of more than one model. Models with shorter temporal timesteps, daily, weekly, or monthly, are better suited than models with annual timesteps to simulate land management effects. A shorter timestep will allow, for example, specific dates of sowing and cropping, and to allow for a specific grazing period. A shorter timestep can also take into account the interaction of the management with climate events and crop stages, for example, an application of slurry a day before a heavy rainfall at an early crop developmental stage with less than full ground cover, which would be expected to promote fast sediment carrying runoff.

2.5.2. Crop type and timing

Crop type and timing are necessary parameters to account for land-use change. SPACSYS accounts for different crop types, seeding date, cultivation/planting schedules, amount, and timing of nutrient amendments. UK-DNDC accounts for crop type, sowing date and density, harvest date, straw management, and irrigation amount. DAYCENT and INCA allow for vegetation type, cultivation/planting schedules, and amount and timing of nutrient amendments. DAISY incorporates a crop planting date and harvest date. RZWQM accounts for crop type, seeding date, and irrigation. APSIM allows for crop rotations. ECOSYS accounts for crop type, seeding and harvest date, type of harvest, and fraction of plant removed.

2.5.3. Livestock grazing/housing periods (including feed input and excreta output)

PASIM, NGAUGE, and $SIMS_{DAIRY}$ are biased to livestock systems. PASIM, HURLEY, OVERSEER, NGAUGE, $SIMS_{DAIRY}$, and SPACSYS consider separate systems of grazing or cut grass. PASIM and $SIMS_{DAIRY}$ consider live weight gain and lactating cow feed intake. $SIMS_{DAIRY}$ also takes into consideration different types of feed supplements, housing date and calculates the associated gaseous emissions from housing and manure storage. NGAUGE considers feed supplements. Diet can modify CH_4 output. CH_4 output is only considered by DAYCENT, ECOSYS, $SIMS_{DAIRY}$, and UK-DNDC/DNDC. PASIM, OVERSEER, NGAUGE, $SIMS_{DAIRY}$, SPACSYS, and MACRO all consider dairy and sheep farming. The HURLEY and OVERSEER pasture models for livestock consider stocking rates.

2.5.4. Nutrient application: Fertilizer and manure

ANIMO, GLEAMS, and DAYCENT include a livestock manure pool for input to nutrient dynamics. MACRO can simulate slurry via an addition to its irrigation component. NGAUGE, INCA, $SIMS_{DAIRY}$, and RZWQM simulate manure additions. SPACSYS simulates nutrient addition via fertilizer and manure applications. It distinguishes between six different types of manure based on their C:N ratios. SPACSYS, NGAUGE, and $SIMS_{DAIRY}$ consider slurry application and distinguish between application by splash plate or injection. NGAUGE and $SIMS_{DAIRY}$ also have an optimization routine for fertilizer rate and timing. ANIMO allows for slurry application, but also additions of fertilizer, manure, and crop residues. A few models like ANIMO, DNDC, NGAUGE, and SIMSDAIRY also consider soil N input by atmospheric deposition of N. DNDC simulates application date and amount of NO_3^-, NH_4^+, NH_3 and urea, and manure. DAYCENT, ECOSYS, HURLEY, INCA, RZWQM, and DAISY allow for fertilizer application, amount, and date. As mentioned previously, NGAUGE and $SIMS_{DAIRY}$ have monthly timesteps, ANIMO can have a daily or weekly timestep, MACRO can have a daily or hourly timestep, HURLEY has an hourly timestep, and the rest of the models have a daily timestep, which renders them all applicable for simulating fertilizer and manure management.

2.5.5. Tillage and other physical modification of land

ANIMO, ECOSYS, RZWQM, and SPACSYS simulate tillage. DNDC simulates tilling date and depth. As with SPACSYS, the GLEAMS tillage module incorporates crop residue, animal waste, and fertilizer, and mixes the respective pools in the ploughed layers. DAISY requires tillage date and method. All of these models have a daily timestep.

2.6. Ease of use for the operator

Logically, the more simplistic models with larger temporal and spatial scale, that is, NOPOLU, MONERIS, REALTA, have lower data requirements than finer scale and more complex process-based models like ANIMO. The lower the data requirements the smaller the workload and the quicker an operator would be able to learn to simulate nutrient output, as a large part of model run would simply consist of data collection. If detail and accuracy are not paramount and general trends are required with a limited budget and timeframe, this type of model may be the one most suitable. The most detailed model included in this chapter is ECOSYS. If a detailed spatial scale or timestep is needed, this terrestrial ecosystem model will usually suffice. The model can also be applied regionally and over long time periods, up to centuries. It has a longer list of parameter requirements of any models

considered in this chapter. To speed data access, several models are now linked into a GIS, accessing a national database. PSYCHIC uses this approach to predict P and sediment transport, accessing a database common to Agriculture Development and Advisory Service (ADAS) users where it was developed. The next step is a web-based public access database, which BASINS uses. BASINS makes it possible to quickly assess large amounts of point source and nonpoint source data in a format that is easy to use and understand. Installed on a personal computer, BASINS allows the user to assess water quality at selected stream sites or throughout an entire watershed. It integrates environmental data, analytical tools, and modeling programs for a cost-effective approach to watershed management. BASINS integrates national databases (elevation, hydrography, meteorological, land use, and soil), assessment tools, data management and graphing programs with models (HSPF, SWAT, PLOAD, and AQUATOX), and analysis tools. HSPF is a watershed hydrology and pollutant transport model (Whittemore and Beebe, 2000) and is the core watershed model in BASINS. A custom GIS interface for BASINS is available in ArcGIS through a toolbar. The program invokes web data download for US databases of hydrologic units across the US available online. This, however, somewhat limits the applicability to other countries. HSPF uses BASINS to extract soil, land cover, and geomorphological data and parameter values from geographic information databases, using the BASINS GIS analysis tools (US Environmental Protection Agency, 2001).

2.7. Spatial scale and temporal timestep

2.7.1. Spatial scale

Spatially most models we reviewed are field scale, for example, SPACSYS, PASIM, DAISY, ANIMO, which meet the requirements for this study (Table 2a). Some models have more than one scale: ECOSYS simulates from field up to regional scale; PSYCHIC is at field and catchment scales; SOMM from plot to global scale; MODCOU from plot to regional scale; and UK-DNDC/DNDC which operate at field or regional scales. The models which work on a catchment scale are generally those whose main focus is stream loading of nutrients, for example, BASINS, EVENFLOW, INCA, MONERIS, NOPOLU, SOURCE AP. In the models looked at, only $SIMS_{DAIRY}$ and OVERSEER were farm scale, incorporating livestock housing and associated emissions and nutrient loss.

2.7.2. Temporal timestep

Most models reviewed worked with a daily temporal scale. Models based on a monthly scale are CNSP, NGAUGE, $SIMS_{DAIRY}$ and PSYCHIC. Daily and monthly timesteps mean a model has the potential to simulate farm management decisions and can reflect monthly variability in weather

(precipitation, temperature). Large timescale models considering over a hundred years are the annual MONERIS, REALTA, NOPOLU, SOURCE AP, and organic matter turnovers in SOMM and HURLEY Pasture are also on a large timescale. On the issue of temporal scale, OVERSEER would be potentially a good agricultural management tool if it had a finer temporal scale. It has been developed for livestock systems, incorporating stocking, fertilizer and manure management operations, but it operates with annual quantities, so the climate does not have a separate wet or dry season, and with an annual scale individual weather events, no matter how extreme, are missed. Models that give results on an annual basis are not really applicable for diffuse water pollution, unless annual pollutant load is the target output. If linked to a streamflow model, a smaller scale could help produce frequencies of exceedance of pollutant concentration and loads. MOTOR is a specialized model based on reaction kinetics, with output expressed in terms of reaction rates of pool components converted in milligram per kilogram of soil, its timestep is not specified explicitly in documentation (Whitmore, 2007) but is inferred that it is daily.

Models which have variable scales are: ECOSYS with a timescale which runs from hourly to centuries; ANIMO with daily to weekly scales; MAGEC which is daily and its SUNDIAL monthly counterpart; and MACRO which runs hourly to daily. NGAUGE and $SIMS_{DAIRY}$ are monthly and annual models.

3. Conclusions

While no model will incorporate all our requirements, there are some that will accommodate more than most. In practice, we have to make some assumptions and accept the limitations of whatever model we use. Thus, we look for a reasonably detailed, flexible, and integrated model with a robust, validated approach and yet one where the processes are explicit.

If we compare which of these models outputs both N_2O emission and NO_3^- leaching, both processes are common to PASIM, DAYCENT, NGAUGE, $SIMS_{DAIRY}$, RZWQM, and SPACSYS. This would make these six models good candidates for assessing secondary effects of mitigation and adaptation, and all output on shorter daily/monthly timescales for field or farm. It is our opinion that when diffuse pollution and its mitigation is considered, taking into account the balance between gaseous emissions of N and leached or overland flow of N, creates an integrated and holistic assessment of the problem. Additionally, DAYCENT and $SIMS_{DAIRY}$ include P cycling.

Of the six models, DAYCENT, PASIM, RZWQM, and SPACSYS incorporate organic turnover which is integral with nitrogen cycling and makes for a more accurate process simulation attuned to biomass dynamics

than empirical studies based on experimental results. All four of these models take in daily climate data and include water movement through the soil.

PASIM, DAYCENT, and SPACSYS consider root dynamics and root: shoot ratio which affects nutrient uptake capacity with decreased precipitation. For land management, PASIM, biased toward dairy farming, considers grazing or cut grass, animal weight, and intake by the lactating cow; however, it is a pasture model so cannot account for a change of land use, such as a different crop or a rotation. Whereas DAYCENT is biased toward cropping and considers vegetation type, cultivation/planting schedules, amount and timing of nutrient amendments, such as fertilizer application. SPACSYS applicable to both livestock and cropping considers tillage, vegetation type, cultivation/planting schedules, amount and timing of nutrient amendments, fertilizer application, cut grass or grazed grass.

In summary, it can be concluded that no single model incorporates all our stated requirements, there were, however, three models, DAYCENT, PASIM, and SPACSYS which would accommodate most features, and would be candidates for further development in the light of our current and future modeling requirements.

Appendix. Brief Description of Selected Models

The Dutch ANIMO model aims to quantify the relation between fertilization level, soil management, and the leaching of nutrients to groundwater and surface water systems for a wide range of soil types and different hydrological conditions (Schoumans and Silgram, 2003). The model was developed in 1985 to evaluate N losses and later the P cycle (organic and inorganic) was added (Groenendijk and Kroes, 1999). The model ANIMO is a functional model incorporating simplified formulations of processes. The organic matter cycle plays an important role for the assessment of long-term effects of land-use changes and fertilization strategies.

APSIM, the Agricultural Production Systems Simulator (Keating *et al.*, 2001), component-based design allows individual models to interact via a common communications protocol on a daily timestep. It was produced for agricultural systems, but the models can simulate many major crop, pasture, and tree species as well as the main soil processes affecting agricultural systems (e.g., water, C, N, and phosphorus dynamics, and erosion) including denitrification and N_2O emissions. (Huth *et al.*, 2010) used APSIM to determine the likely production of N_2O emissions from leguminous crop residues when incorporating legumes into cereal crop rotations.

BASINS is a multipurpose environmental analysis system designed for use by regional, state, and local agencies in performing watershed and water quality-based studies. The model is connected to a GIS interface which links with large US databases for data input (Mohamoud *et al.*, 2009).

CNSP (McCaskill and Blair, 1990) developed for C, N, S, and P dynamics in white clover pastures is very focused on nutrient uptake, root simulation and includes mycorrhizal effects. It is a specialist model that focuses on soil nutrient dynamics.

DAISY is a soil–plant–atmosphere model (Hansen *et al.*, 1991). It is a single column model, which describes crop growth, water and heat balances, as well as the dynamics of organic matter, ammonium, and nitrate in an agricultural ecosystem. It is based on management practices as well as soil and weather data.

DAYCENT is the daily timestep version of the CENTURY biogeochemical model (Parton, 1996; Parton *et al.*, 1987). DAYCENT simulates fluxes of C and N among the atmosphere, vegetation, and soil (Parton *et al.*, 1998, 2001). Key submodels include soil water content and temperature by layer, plant production and allocation of net primary production, decomposition of litter and soil organic matter, mineralization of nutrients, N gas emissions from nitrification and denitrification, and CH_4 oxidation in nonsaturated soils. DAYCENT model considers sorbed soil P in equilibrium with a labile soil P from which leaching occurs, and P loss through soil erosion. DAYCENT accounts for soil class, daily weather, historical vegetation cover, and land management practices such as crop type, fertilizer additions, and cultivation events.

The ECOSYS model of natural and managed ecosystems is a comprehensive model with detailed processes concerning N_2O and captures the large temporal variability of N_2O at high temporal and spatial resolution, under site-specific conditions such as climate, soil type, land use, topography, etc (Grant, 1995). The model can simulate the transport and transformation of heat, water, C, O_2, N, P, and ionic solutes through soil–plant–atmosphere systems with the atmosphere as the upper boundary and soil parent material as the lower boundary (Metivier *et al.*, 2009).

The European Soil Erosion Model (EUROSEM; Morgan *et al.*, 1998) is a sediment transport, erosion, and deposition model simulating transport over the land surface by rill and interill processes in single storms for both individual fields and small catchments. Model output includes total runoff, total soil loss, the storm hydrograph, and storm sediment graph. Although a specialist model, it has the potential to be linked with other models. Compared with other erosion models, EUROSEM has explicit simulation of interill and rill flow; plant cover effects on interception and rainfall energy; rock fragment (stoniness) effects on infiltration, flow velocity and splash erosion; and changes in the shape and size of rill channels as a result of erosion and deposition.

The quantification tool EVENFLOW (Schoumans and Silgram, 2003) is a catchment model that simulates the loss of nitrate in soil drainage and the routing of leachate through a catchment system. The system uses statistical data on land use, farming practices, climate, and soil characteristics as inputs, collated at a spatial resolution of 1 km^2. The model was developed to provide a robust estimate of inorganic nitrogen fluxes and concentrations in river waters, primarily originating from agricultural land, for any catchment within England and Wales.

GLEAMS (Leonard *et al.*, 1987) was originally a chemical transport, soil erosion, and runoff model, which developed dynamic nutrient cycling, subsurface drainage flow, macropore flow, and pesticide flow.

HURLEY Pasture (Arah *et al.*, 1997; Thornley and Verberne, 1989) compartmentalizes grass into four different age categories of root and leaf; flows of carbon (C), nitrogen, and water between adjacent compartments occur in response to concentration or water potential gradients across resistances determined by compartment size; structural growth of the various compartments is governed by local substrate concentrations and temperature. Since photosynthesis varies rapidly, the fundamental timestep is short (around 15 min for stability); appropriate input data are generated from available measurements assuming sinusoidal diurnal (and, if necessary, seasonal) waves.

INCA—Integrated Nitrogen in Catchments model (Wade *et al.*, 2002; Whitehead *et al.*, 1998)—is a process-based model of the nitrogen cycle in the plant/soil and instream systems. The model simulates the nitrogen export from different land-use types within a river system, and the instream nitrate and ammonium concentrations at a daily timestep. The interface permits multiple crop and vegetation growth periods and fertilizer applications. It is able to reproduce the seasonal dynamics observed in streamwater nitrogen concentration data, and the loads associated with plant/soil system nitrogen processes (Wade *et al.*, 2002).

MACRO (Jarvis, 1994; McGechan *et al.*, 2008) is a nonsteady-state water movement and solute transport model for macroporous layered soils, which couples unsaturated–saturated flow with root water uptake and a drain system and has a separate representation of processes in "macropores" and soil matrix "micropores." In earlier versions of the model, only soluble contaminants were considered, and applications concerned mainly water contamination by pesticides. However, MACRO later (Jarvis *et al.*, 1999) included a representation of colloid-facilitated contaminant transport, a process particularly relevant to phosphorus pollution.

The MAGEC soil model (Smith *et al.*, 2006) for crop growth and yield in response to global environmental changes was adapted from SUNDIAL (Bradbury *et al.*, 1993; Bradbury and Powlson, 1994; Smith *et al.*, 1996). The soil organic matter pools were modified so that they exactly corresponded to the pools used in a well-established soil carbon model, RothC (Coleman and Jenkinson, 1996; Jenkinson and Coleman, 1994).

The timestep of the monthly SUNDIAL was altered in MAGEC to a daily timestep. Underlying physiological processes include photosynthesis, transpiration, nitrogen uptake, partitioning of biomass and nitrogen among growing organs, phenology, leaf area development and senescence, and root extension.

MODCOU is a spatially distributed hydrological model used to simulate the surface runoff and groundwater flow in multilayered hydrological systems (Korkmaz *et al.*, 2009; Ledoux *et al.*, 2002). It consists of several components, namely, surface model, groundwater model, unsaturated zone model, and the coupled model. Spatial information on the basin is extracted by using digital elevation model (DEM) analysis, and operations are carried out via a GIS interface.

The MONERIS (Venohr *et al.*, 2005) model was developed for the nutrient inputs via various points and diffuse pathways in German river basins. The basis for the model is data on runoff and water quality from river catchment studies and physical data from a GIS. There are at least four different diffuse paths to consider: direct nutrient input on the water by atmospheric deposition, nutrient input into the river by surface runoff, input via interflow which represents a fast subsurface flow component, and input via base flow (groundwater). Inputs of dissolved substances via surface runoff and entries of bound nutrients and suspended particulate matter via erosion are distinguished.

MOTOR (Modular description of the Turnover of Organic matter; Whitmore, 2007; Whitmore *et al.*, 1997) describes the transformation of organic carbon and nutrients in soil. The state of each component of the organic matter in soil is described by a vector and the transformations by a matrix of terms. Actual turnover is calculated by multiplication of these matrices, state vectors, and a rate vector. The resulting system is powerful because it is modular in construction and any one part of it may be altered simply and quickly without reference to the rest of the calculation system (Whitmore, 2007). The model derives from an earlier body of various works and an earlier version of MOTOR (Whitmore *et al.*, 1997) which incorporated the Verberne organic matter turnover model (Verberne *et al.*, 1990), and MOTOR has been influenced by SUNDIAL (Bradbury *et al.*, 1993) and the Hassink and Whitmore model of C flows (Hassink and Whitmore, 1997).

NGAUGE (Brown *et al.*, 2005) is an empirically based model of N cycling in grassland soils based on published multisite grassland data sets. It includes an optimization procedure to identify a fertilizer amount and distribution according to the criteria of herbage production and N losses to the environment. It is an improvement on existing nitrogen fertilizer recommendation systems in that it relates production to environmental impact and is therefore potentially valuable to policy makers and researchers for identifying pollution mitigation strategies.

NOPOLU (European Environment Agency/IFEN, 2000; Schoumans and Silgram, 2003) is an agricultural diffuse emissions module as part of a comprehensive catchment description database. It appears to avoid the issue of soil processes altogether by retrieving agricultural statistical data and processing it with land cover data to make it more relevant, and incorporating runoff data.

OVERSEER is a farmscale model that develops budgets for major soil nutrients (N, P, K, S, Ca, Mg, and Na) for most NZ farming enterprises (Ledgard *et al*., 1999; Wheeler *et al*., 2008). The primary purpose of the model is to prepare reports from which the user can make decisions on nutrient requirements for a farm and/or blocks of land within a farm. Of interest is the ability to calculate nitrate leaching and on farm emissions of GHGs—CH_4, N_2O, and CO_2.

The pasture simulation model, PASIM, reproduces dry matter production and energy balance of cut temperate grasslands at lowland sites (Riedo *et al*., 2000). It is applicable to climate change, has a snow cover effects simulation, and can be used to determine long-term effects of changes in CO_2 and climate on productivity and total C in the system. It includes root system exudation and uptake. It considers grazing by dairy cows.

PSYCHIC (Davison *et al*., 2008) is a process-based model of phosphorus and SS mobilization in land runoff and subsequent delivery to watercourses. Modeled transfer pathways include release of desorbable soil P, detachment of SS and associated particulate P, incidental losses from manure and fertilizer applications, losses from hard standings. Further, it includes the transport of all the above to watercourses in subsurface drainage (where present) and via surface pathways, and losses of dissolved P from point sources. The model can operate at two spatial scales, although the scientific core is the same in both cases. At catchment scale, the model uses easily available national scale datasets to infer all necessary input data, while at field scale, the user is required to supply all necessary data.

The Irish model, called REALTA (Kirk McClure Morton Engineering Consultants, 2001; Magette, 1998), uses a self-developed procedure for estimating losses from agriculture based on actual measurements obtained from catchment monitoring and management systems (Schoumans and Silgram, 2003). The procedure takes on board detailed knowledge of physical conditions and farming practices in the catchment. Percentage loss figures, initially derived from detailed agricultural studies at mini-catchment and subcatchment level, are linked to an agricultural risk map. Estimated nutrient percentage loss figures can be applied to the total agricultural import to produce an overall estimate for the total agricultural nutrient losses to surface waters.

RZWQM (root zone water quality model; Ma *et al*., 2001) is an agricultural system model, simulating agricultural production and environmental quality. A nutrient module simulates carbon and nitrogen transformations in the soil profile. It comprises plant growth, water movement, heat transport, C and N dynamics, chemical transport, and management practices.

SIMS$_{DAIRY}$ (Del Prado *et al.*, 2006; Del Prado and Scholefield, 2008) is a farm scale model whose N cycling core is based on NGAUGE with strategic management operations included and an optimization procedure to maximize herbage production or minimize N losses to the environment. It has added indices for biodiversity, animal welfare, and farm economics and has an added P submodel from PSYCHIC.

SOILN (Eckersten *et al.*, 1996) was designed to simulate N transport and transformations in soils and its uptake by plants. The SOILN model includes all the major processes determining the inputs (fertilizer and manure, atmospheric deposition), transformation linked to C cycle (mineralization and immobilization), and outputs (leaching, denitrification, harvest yield). SOILN must be carried out in conjunction with the soil water and heat model SOIL (Janssen, 1998). A simulation with SOIL, which must be carried out prior to a simulation with SOILN, requires input data representing weather parameters including temperature, radiation (or sunshine hours), wind speed, and precipitation.

SOMM (Chertov *et al.*, 1995) is a specialized soil organic matter decomposition model. Originally designed for forest soils, it has since been used for Rothamsted Park Grass soil. It presents organic matter decomposition in three stages, using five mass and five N compartments. At the first stage, part of the litter layer (L pool) is set to be lost through biochemical degradation and fermentation thereby contributing to the fermentation layer (F pool). At the second stage, the fermented organic matter is lost through heterotrophic respiration and transformed into humus (H pool). At this stage, fermented matter is digested by microbial organisms, and soil mesofauna (e.g., earthworms), both producing humus. At each stage, the rates of the litter mineralization, fermentation, and humification are empirically related to the ash and N content of the decaying litter, and to local soil temperature and moisture estimates (Zhang *et al.*, 2008).

SOURCE AP (National Environmental Research Institute, 2000), the source apportionment method quantification tool, does not consider soil processes but can nonetheless serve as a tool to assess pollutant loads at catchment level if used in conjunction with another model. It quantifies nutrient losses from diffuse sources such as agricultural land, forest and pristine area, estimated as the difference between the transport and the measured emission (Schoumans and Silgram, 2003).

SPACSYS (Soil Plant Atmosphere Continuum System) is a multilayer, field scale, weather-driven, and daily timestep dynamic simulation model. It includes a plant growth component; an N cycling component; a water component, which includes representation of water flow to field drains as well as downward through the soil layers; and an energy component. Equations for soil water processes and heat transformation are almost identical to those in the SOIL model (Janssen, 1998). It is a plant growth and soil nutrient system that adds root dynamics, central to the study of plant growth

and development, C and nutrient cycling, and water movement within the plant/soil system (Wu *et al.*, 2007).

UK-DNDC is inherited from the earlier version DNDC model. It was originally developed for predicting carbon sequestration and trace gas emissions from upland agroecosystems (Li *et al.*, 1997). The core of the model is a mechanistic simulation of soil C and N biogeochemistry, developed to assess N_2O, NO, N_2, NH_3, and CO_2 emissions. DNDC was modified for application to the UK and called UK-DNDC. UK-specific input data were added to DNDC's database and the ability to simulate daily C and N inputs from grazing animals and applied animal waste was added to the model. Validation of the model at the field scale shows that predictions of N_2O emission match observations well (Brown *et al.*, 2002). Since the original development of UK-DNDC, both of these models have developed separately.

The early version of DNDC (Li *et al.*, 1997) is organized as four interrelated modules for soil and climate, crop growth decomposition, and denitrification. This is the version that UK-DNDC (Brown *et al.*, 2002) uses. The soil climate submodel calculates hourly and daily soil temperature, moisture, and heat flows. The crop growth submodel simulates crop biomass accumulation and partitioning based on thermal degree days and daily N and water uptake. The decomposition submodel calculates decomposition, nitrification, NH_3 volatilization, and CO_2 production on a daily timestep. The denitrification submodel tracks the sequential biochemical reductions from nitrate (NO_3).

DNDC (Zhang *et al.*, 2002) updated to add crop genetic parameters, atmospheric CO_2 concentration, SCS curve number for surface runoff, and average water table depth.

DNDC continued in its development. DNDC (Li *et al.*, 2010) now consists of six submodels for simulating soil climate, plant growth, decomposition, nitrification, denitrification, and fermentation.

DNDC is used worldwide. The authors recognize that there are differences between UK-DNDC/the earlier and later versions of DNDC, however, the basis they are built upon and applicability are similar. To avoid repetition, they have chosen to describe one model instead of two throughout the text, referring to the UK-DNDC model (an example of how original models are adapted by researchers for specific purposes) which incorporates the earlier version of DNDC.

REFERENCES

Amelung, W., Brodowski, S., Sandhage-Hofmann, A., and Bol, R. (2008). Combining biomarker with stable isotope analyses for assessing the transformation and turnover of soil organic matter. *In* "Advances in Agronomy", Vol. 100, pp. 155–250. Elsevier Academic Press Inc., San Diego.

Arah, J. R. M., Thornley, J. H. M., Poulton, P. R., and Richter, D. D. (1997). Simulating trends in soil organic carbon in long-term experiments using the ITE (Edinburgh) Forest and Hurley Pasture ecosystem models. *Geoderma* **81,** 61–74.

Basset, A. (2010). Aquatic science and the water framework directive: A still open challenge towards ecogovernance of aquatic ecosystems. *Aquat. Conserv.: Mar. Freshw. Ecosyst.* **20,** 245–249.

Beauchemin, K. A., Janzen, H. H., Little, S. M., McAllister, T. A., and McGinn, S. M. (2010). Life cycle assessment of greenhouse gas emissions from beef production in western Canada: A case study. *Agric. Syst.* **103,** 371–379.

Beman, J. M., Arrigo, K. R., and Matson, P. A. (2005). Agricultural runoff fuels large phytoplankton blooms in vulnerable areas of the ocean. *Nature* **434,** 211–214.

Bergstrom, L., Johnsson, H., and Torstensson, G. (1991). Simulation of soil-nitrogen dynamics using the soil model. *Fertil. Res.* **27,** 181–188.

Blackwell, M. S. A., Brookes, R. C., de la Fuente-Martinez, N., Gordon, H., Murray, P. J., Snars, K. E., Williams, J. K., Bol, R., and Haygarth, P. M. (2010). Phosphorus solubilization and potential transfer to surface waters from the soil microbial biomass following drying-rewetting and freezing-thawing. *In* "Advances in Agronomy", Vol. 106, pp. 1–35. Elsevier Academic Press Inc., San Diego.

Boegh, E., Thorsen, M., Butts, M. B., Hansen, S., Christiansen, J. S., Abrahamsen, P., Hasager, C. B., Jensen, N. O., van der Keur, P., Refsgaard, J. C., Schelde, K., Soegaard, H., *et al.* (2004). Incorporating remote sensing data in physically based distributed agro-hydrological modelling. *J. Hydrol.* **287,** 279–299.

Bol, R., Poirier, N., Balesdent, J., and Gleixner, G. (2009). Molecular turnover time of soil organic matter in particle-size fractions of an arable soil. *Rapid Commun. Mass Spectrom.* **23,** 2551–2558.

Bond-Lamberty, B., and Thomson, A. (2010). Temperature-associated increases in the global soil respiration record. *Nature* **464,** 579–582.

Bradbury, N. J., and Powlson, D. S. (1994). The potential impact of global environmental change on nitrogen dynamics in arable systems. *In* "Soil Responses to Climate Change" (M. D. A. Rounsevell and P. J. Loveland, Eds.), NATO ASI Series **123,** pp. 137–153. Springer-Verlag, Berlin.

Bradbury, N. J., Whitmore, A. P., Hart, P. B. S., and Jenkinson, D. S. (1993). Modeling the fate of nitrogen in crop and soil in the years following application of N-15-labeled fertilizer to winter-wheat. *J. Agric. Sci.* **121,** 363–379.

Brown, L., Syed, B., Jarvis, S. C., Sneath, R. W., Phillips, V. R., Goulding, K. W. T., and Li, C. (2002). Development and application of a mechanistic model to estimate emission of nitrous oxide from UK agriculture. *Atmos. Environ.* **36,** 917–928.

Brown, L., Scholefield, D., Jewkes, E. C., Lockyer, D. R., and Del Prado, A. (2005). NGAUGE: A decision support system to optimise N fertilisation of British grassland for economic and environmental goals. *Agric. Ecosyst. Environ.* **109,** 20–39.

Bryant, J. R., and Snow, V. O. (2008). Modelling pastoral farm agro-ecosystems: A review. *N.Z. J. Agric. Res.* **51,** 349–363.

Bust, T. P., and Haycock, N. E. (1993). Controlling losses of nitrate by changing land use. John Wiley & Sons Ltd., Chichester, UK.

Cardenas, L. M., Thorman, R., Ashleee, N., Butler, M., Chadwick, D., Chambers, B., Cuttle, S., Donovan, N., Kingston, H., Lane, S., Dhanoa, M. S., and Scholefield, D. (2010). Quantifying annual N2O emission fluxes from grazed grassland under a range of inorganic fertiliser nitrogen inputs. *Agric. Ecosyst. Environ.* **136,** 218–226.

Chadwick, D. R., John, F., Pain, B. F., Chambers, B. J., and Williams, J. (2000). Plant uptake of nitrogen from the organic nitrogen fraction of animal manures: A laboratory experiment. *J. Agric. Sci.* **134,** 159–168.

Challinor, A. J., Ewert, F., Arnold, S., Simelton, E., and Fraser, E. (2009). Crops and climate change: Progress, trends, and challenges in simulating impacts and informing adaptation. *J. Exp. Bot.* **60,** 2775–2789.

Chertov, O. G., Komarov, A. S., Crocker, G., Grace, P., Klir, J., Korschens, M., Poulton, P. R., and Richter, D. (1995). Simulating trends of soil organic carbon in seven long-term experiments using the SOMM model of the humus types, pp. 121–135. Harpenden, England.

Coleman, K., and Jenkinson, D. S., (Eds.) (1996). *In* "RothC-26.0033—A Model for the turnover of carbon in soil". , pp. 237–246. Springer-Verlag, Heidelberg, Germany.

Collins, A. L., and McGonigle, D. F. (2008). Monitoring and modelling diffuse pollution from agriculture for policy support: UK and European experience. *Environ. Sci. Policy* **11,** 97–101.

Cooter, E. J., Bash, J. O., Walker, J. T., Jones, M. R., and Robarge, W. (2010). Estimation of NH3 bi-directional flux from managed agricultural soils. *Atmos. Environ.* **44,** 2107–2115.

Cuellar, A. D., and Webber, M. E. (2008). Cow power: The energy and emissions benefits of converting manure to biogas. *Environ. Res. Lett.* **3,** 034002.

Cuttle, S. P., Macleod, C. J. A., Chadwick, D. R., Scholefield, D., Haygarth, P. M., Newell-Price, P., Harris, D., Shepherd, M. A., Chambers, B. J., and Humphrey, R. (2007). An inventory of measures to control diffuse water pollution from agriculture. Report to Defra, produced by ADAS and IGER, London.

Davison, P. S., Withers, P. J. A., Lord, E. I., Betson, M. J., and Stromqvist, J. (2008). PSYCHIC—A process-based model of phosphorus and sediment mobilisation and delivery within agricultural catchments. Part 1: Model description and parameterisation. *J. Hydrol.* **350,** 290–302.

DeBusk, W. F., White, J. R., and Reddy, K. R. (2001). Carbon and nitrogen dynamics in wetland soils. *In* "Modelling Carbon and Nitrogen Dynamics for Soil Management" (M. J. Shaffer, L. Ma, and S. Hansen, Eds.), Lewis, Boca Raton.

Defra. (2009). Safeguarding our soils. A strategy for England. Rep. No. Defra Report PB13297.

DeJong, R., and Bootsma, A. (1996). Review of recent developments in soil water simulation models. *Can. J. Soil Sci.* **76,** 263–273.

Del Grosso, S. J., Ojima, D. S., Parton, W. J., Stehfest, E., Heistemann, M., DeAngelo, B., and Rose, S. (2009). Global scale DAYCENT model analysis of greenhouse gas emissions and mitigation strategies for cropped soils. *Glob. Planet. Change* **67,** 44–50.

Del Prado, A., and Scholefield, D. (2008). Use of SIMSDAIRY modelling framework system to compare the scope on the sustainability of a dairy farm of animal and plant genetic-based improvements with management-based changes. *J. Agric. Sci.* **146,** 195–211.

Del Prado, A., Scholefield, D., Chadwick, D., Misselbrook, T., Haygarth, P., Hopkins, A., Dewhurst, R., Jones, R., Moorby, J., Davison, P., Lord, E., Turner, M., *et al.* (2006). A modelling framework to identify new integrated dairy production systems. *In* "Sustainable Grassland Productivity: Proceedings of the 21st General Meeting of the European Grassland Federation," pp. 766–768. Badajoz, Spain, 3–6 April, 2006. Sociedad Espanola para el Estudio de los Pastos (SEEP).

Del Prado, A., Chadwick, D., Cardenas, L., Misselbrook, T., Scholefield, D., and Merino, P. (2010). Exploring systems responses to mitigation of GHG in UK dairy farms. *Agric. Ecosyst. Environ.* **136,** 318–332.

DeRamus, H. A., Clement, T. C., Giampola, D. D., and Dickison, P. C. (2003). Methane emissions of beef cattle on forages: Efficiency of grazing management systems. *J. Environ. Qual.* **32,** 269–277.

Dils, R., Leaf, S., Robinson, R., and Sweet, N. (2001). Phosphorus in the environment—Why should recovery be a policy issue? Environment Agency, 2nd international conference on the recovery of phosphorus from sewage and animal wastes. 12–13 March 2001, Noordwijkerhout. CEEP (Comite European d'etudes des polyphosphates).

Eckersten, H., Janssson, P. E., and Johnsson, H. (1996). SOILN Model, User's Manual. 3rd edn., Swedish University of Agricultural Sciences, Department of Soil Sciences, Uppsala. Rep. No. Comm. 96:1.

European Environment Agency/IFEN. (2000). Calculation of nutriment surplus from agricultural sources. Statistics spatialisation by means of CORINE Land Cover. Application to the case of Nitrogen.

Fey, R., Zoz, T., Steiner, F., Richart, A., and Brito, O. R. (2010). Leaching of nitrogen in column in regarding soil particle size. *Scientia Agraria* **11,** 181–185.

Fraser, I., and Stevens, C. (2008). Nitrogen deposition and loss of biological diversity: Agricultural land retirement as a policy response. *Land Use Policy* **25,** 455–463.

Froschl, L., Pierrard, R., and Schonback, W. (2008). Cost-efficient choice of measures in agriculture to reduce the nitrogen load flowing from the Danube River into the Black Sea An analysis for Austria, Bulgaria, Hungary and Romania. *Ecol. Econ.* **68,** 96–105.

Gifford, R. M., Campbell, B. D., and Howden, S. M. (1996). Options for adapting agriculture to climate change: Australian and New Zealand examples. CSIRO, East Melbourne.

Gilmanov, T. G., Aires, L., Barcza, Z., Baron, V. S., Belelli, L., Beringer, J., Billesbach, D., Bonal, D., Bradford, J., Ceschia, E., Cook, D., Corradi, C., *et al.* (2010). Productivity, respiration, and light-response parameters of world grassland and agroecosystems derived from flux-tower measurements. *Rangeland Ecol. Manage.* **63,** 16–39.

Giltrap, D. L., Li, C. S., and Saggar, S. (2010). DNDC: A process-based model of greenhouse gas fluxes from agricultural soils. *Agric. Ecosyst. Environ.* **136,** 292–300.

Granger, S. J., Bol, R., Butler, P., Haygarth, P. M., Naden, P., Old, G., Owens, P. N., and Smith, B. P. G. (2007). Processes affecting transfer of sediment and colloids, with associated phosphorus, from intensively farmed grasslands: Tracing sediment and organic matter. *Hydrol. Process.* **21,** 417–422.

Granger, S. J., Bol, R., Anthony, S., Owens, P. N., White, S. M., and Haygarth, P. M. (2010a). Towards a holistic classification of diffuse agricultural water pollution from intensively managed grasslands on heavy soils. *Adv. Agron.* **105,** 83–115.

Granger, S. J., Hawkins, J. M. B., Bol, R., White, S. M., Naden, P., Old, G., Bilotta, G. S., Brazier, R. E., Macleod, C. J. A., and Haygarth, P. M. (2010b). High temporal resolution monitoring of multiple pollutant responses in drainage from an intensively managed grassland catchment caused by a summer storm. *Water Air Soil Pollut.* **205,** 377–393.

Grant, R. F. (1995). Dynamics of energy, water, carbon and nitrogen in agricultural ecosystems—Simulation and experimental validation. *Ecol. Modell.* **81,** 169–181.

Grant, R. F. (1997). Changes in soil organic matter under different tillage and rotation: Mathematical modeling in ecosys. *Soil Sci. Soc. Am. J.* **61,** 1159–1175.

Grant, R. F., Pattey, E., Goddard, T. W., Kryzanowski, L. M., and Puurveen, H. (2006). Modeling the effects of fertilizer application rate on nitrous oxide emissions. *Soil Sci. Soc. Am. J.* **70,** 235–248.

Groenendijk, P., and Kroes, J. G. (1999). Modelling the nitrogen & phosphorus leaching to groundwater and surface water, ANIMO 3.5. Winand-Staring Centre, Wageningen, Netherlands.

Hansen, S., Jensen, H. E., Nielsen, N. E., and Svendsen, H. (1991). Simulation of nitrogen dynamics and biomass production in winter-wheat using the Danish simulation-model daisy. *Fertil. Res.* **27,** 245–259.

Hassink, J., and Whitmore, A. P. (1997). A model of the physical protection of organic matter in soils. *Soil Sci. Soc. Am. J.* **61,** 131–139.

Hawkins, J. M. B., and Scholefield, D. (1996). Molybdate-reactive phosphorus losses in surface and drainage waters from permanent grassland. *J. Environ. Qual.* **25,** 727–732.

Heathwaite, A. L. (2010). Multiple stressors on water availability at global to catchment scales: Understanding human impact on nutrient cycles to protect water quality and water availability in the long term. *Freshw. Biol.* **55,** 241–257.

Horrigan, L., Lawrence, R. S., and Walker, P. (2002). How sustainable agriculture can address the environmental and human health harms of industrial agriculture. *Environ. Health Perspect.* **110,** 445–456.

Huth, N. I., Thorburn, P. J., Radford, B. J., and Thornton, C. M. (2010). Impacts of fertilisers and legumes on N2O and CO2 emissions from soils in subtropical agricultural systems: A simulation study. *Agric. Ecosyst. Environ.* **136,** 351–357.

Janssen, P. E. (1998). Simulation Model for Soil Water and Heat Conditions. Description of the SOIL Model. Division of Agricultural Hydrotechnics, Communications 98:2, Swedish University of Agricultural Sciences, Uppsala.

Janzen, H. H., Angers, D. A., Boehm, M., Bolinder, M., Desjardins, R. L., Dyer, J. A., Ellert, B. H., Gibb, D. J., Gregorich, E. G., Helgason, B. L., Lemke, R., Masse, D., *et al.* (2006). A proposed approach to estimate and reduce net greenhouse gas emissions from whole farms. *Can. J. Soil Sci.* **86,** 401–418.

Jarvis, N. (1994). The MACRO Model—Technical Description and Sample Simulations. Department of Soil Sciences, Swedish University of Agricultural Sciences, Uppsala. Rep. No. Reports and Dissertations 19, 51 pp.

Jarvis, S. C., Barraclough, D., Williams, J., and Rook, A. J. (1991). Patterns of denitrification loss from grazed grassland—Effects of N fertilizer inputs at different sites. *Plant Soil* **131,** 77–88.

Jarvis, N. J., Villholth, K. G., and Ulen, B. (1999). Modelling particle mobilization and leaching in macroporous soil. *Eur. J. Soil Sci.* **50,** 621–632.

Jenkinson, D. S., and Coleman, K. (1994). Calculating the annual input of organic-matter to soil from measurements of total organic-carbon and radiocarbon. *Eur. J. Soil Sci.* **45,** 167–174.

Keating, B. A., Gaydon, D., Huth, N. I., Probert, M. E., Verburg, K., Smith, C. J., and Bond, W. (2001). Use of modelling to explore the water balance of dryland farming systems in the Murray-Darling Basin, Australia. *J. Agron.* **18,** 159–169.

Kersebaum, K. C., Hecker, J. M., Mirschel, W., and Wegehenkel, M. (2007). Modelling water and nutrient dynamics in soil-crop systems: A comparison of simulation models applied on common data sets. Springer, Dordrecht.

Kirk McClure Morton Engineering Consultants (2001). The Lough Derg and Lough Ree Catchment Monitoring and Management System. Final Report.

Korkmaz, S., Ledoux, E., and Onder, H. (2009). Application of the coupled model to the Somme river basin. *J. Hydrol.* **366,** 21–34.

Kronvang, B., Rubaek, G. H., and Heckrath, G. (2009). International phosphorus workshop: Diffuse phosphorus loss to surface water bodies-risk assessment, mitigation options, and ecological effects in river basins. *J. Environ. Qual.* **38,** 1924–1929.

Lal, R. (2004). Soil carbon sequestration impacts on global climate change and food security. *Science* **304,** 1623–1627.

Lal, R. (2010). Beyond Copenhagen: Mitigating climate change and achieving food security through soil carbon sequestration. *Food Security* **2,** 169–177.

Landsberg, J. J., Kaufmann, M. R., Binkley, D., Isebrands, J., and Jarvis, P. G. (1991). Evaluating progress toward closed forest models based on fluxes of carbon, water and nutrients. *Tree Physiol.* **9,** 1–15.

Leakey, A. D. B., Ainsworth, E. A., Bernacchi, C. J., Rogers, A., Long, S. P., and Ort, D. R. (2009). Elevated CO2 effects on plant carbon, nitrogen, and water relations: Six important lessons from FACE. *J. Exp. Bot.* **60,** 2859–2876.

Ledgard, S. F., Edgecombe, G. A., and Roberts, A. H. C. (1999). Application of the nutrient budgeting model OVERSEER to assess management options and Regional Council

consent requirements on a Hawke's Bay dairy farm. *In* "Sixty-First Conference," Vol. 61, pp. 227–231. Napier, New Zealand, 5–7 October 1999.

Ledoux, E., Etchevers, P., Golaz, C., Habets, F., Noilhan, J., and Voirin, S. (2002). Regional simulation of the water budget and riverflows with the ISBA-MODCOU coupled model. Application to the Adour and Rhone basins. Water Resources Publications, Colorado.

Leonard, R. A., Knisel, W. G., and Still, D. A. (1987). Gleams—Groundwater loading effects of agricultural management-systems. *Trans. Asae* **30,** 1403–1418.

Lerner, D. N., and Harris, B. (2009). The relationship between land use and groundwater resources and quality. *Land Use Policy* **26,** S265–S273.

Lewis, D. R., and McGechan, M. B. (1999). Watercourse pollution due to surface runoff following slurry spreading. Part I: Calibration of the soil water simulation model SOIL for fields prone to surface runoff. *J. Agric. Eng. Res.* **72,** 275–290.

Lewis, D. R., and McGechan, M. B. (2002). A review of field scale phosphorus dynamics models. *Biosyst. Eng.* **82,** 359–380.

Li, C. S., Frolking, S., Crocker, G. J., Grace, P. R., Klir, J., Korchens, M., and Poulton, P. R. (1997). Simulating trends in soil organic carbon in long-term experiments using the DNDC model. *Geoderma* **81,** 45–60.

Li, S., Jin, X., Fan, X., Huang, W., and Cao, Z. (2010). Ruminant production and carbon emission reduction measures. *Chin. J. Anim. Nutr.* **22,** 2–9.

Lu, Y. Z., Li, B. G., and Cui, Y. (2006). Micro-scale spatial variance of soil nutrients under different plant communities. *Sci. Agric. Sin.* **39,** 1581–1588.

Lu, M., Mao, G., Xiang, S., Zhang, L., Huang, M., and Liu, M. (2009). Study on the characteristics of ammonium nitrogen loss by surface runoff and its numerical simulation in rice-wheat rotation. *Acta Agric. Shanghai* **25,** 43–47.

Ma, L., and Shaffer, M. J. (2001). A review of carbon and nitrogen processes in nine US soil nitrogen dynamics models. *In* "Modelling Carbon and Nitrogen Dynamics for Soil Management" (M. J. Shaffer, L. Ma, and S. Hansen, Eds.), Lewis, Boca Raton.

Ma, L., Shaffer, M. J., and Ahuja, L. R. (2001). Application of RZWQM for soil nitrogen dynamics. *In* "Modelling Carbon and Nitrogen Dynamics for Soil Management" (M. J. Shaffer, L. Ma, and S. Hansen, Eds.), Lewis, Boca Raton.

Magette, W. L. (1998). Factors affecting losses of nutrients from agricultural systems and delivery to water resources. *In* "Draft Guidelines for Nutrient Use in Intensive Agricultural Enterprises" (O. T. Carton, Ed.), pp. 6–31. Teagasc, Wexford.

Malby, A. R., Whyatt, J. A., Timmis, R. J., Wilby, R. L., and Orr, H. G. (2007). Long-term variations in orographic rainfall: Analysis and implications for upland catchments. *Hydrolog. Sci. J.* **52,** 276–291.

Mantovi, P., Fumagalli, L., Beretta, G. P., and Guermandi, M. (2006). Nitrate leaching through the unsaturated zone following pig slurry applications. *J. Hydrol.* **316,** 195–212.

Matthews, R. A., Yamulki, S., Retter, A. L., Donovan, N., Chadwick, D. R., and Jarvis, S. C. (2006). Nitrous oxide and methane emissions from unmanaged wet areas of intensive dairy systems. Vol. II, Aarhus, Denmark, 11–13 September 2006. *In* "12th Ramiran International Conference. Technology for Recycling of Manure and Organic Residues in a Whole-Farm Perspective," pp. 225–228. Danmarks Jordbrugs Forskning.

McCaskill, M. R., and Blair, G. J. (1990). A model of S, P and N uptake by a perennial pasture.1. model construction. *Fertil. Res.* **22,** 161–172.

McGechan, B., and Wu, L. (2001). A review of carbon and nitrogen processes in European soil nitrogen dynamics models. *In* "Modelling Carbon and Nitrogen Dynamics for Soil Management" (M. J. Shaffer, L. Ma, and S. Hansen, Eds.), Lewis, Boca Raton.

McGechan, M. B., Lewis, D. R., and Vinten, A. J. A. (2008). A river water pollution model for assessment of best management practices for livestock farming. *Biosyst. Eng.* **99,** 292–303.

McGinn, S. M., and Shepherd, A. (2003). Impact of climate change scenarios on the agroclimate of the Canadian prairies. *Can. J. Soil Sci.* **83,** 623–630.

Meijide, A., Cardenas, L. M., Sanchez-Martin, L., and Vallejo, A. (2010). Carbon dioxide and methane fluxes from a barley field amended with organic fertilizers under Mediterranean climatic conditions. *Plant Soil* **328,** 353–367.

Melillo, J. M., Aber, J. D., Linkins, A. E., Ricca, A., Fry, B., and Nadelhoffer, K. J. (1989). Carbon and nitrogen dynamics along the decay continuum—Plant litter to soil organic-matter. *Plant Soil* **115,** 189–198.

Metivier, K. A., Pattey, E., and Grant, R. F. (2009). Using the ecosys mathematical model to simulate temporal variability of nitrous oxide emissions from a fertilized agricultural soil. *Soil Biol. Biochem.* **41,** 2370–2386.

Millar, N., Robertson, G. P., Grace, P. R., Gehl, R. J., and Hoben, J. P. (2010). Nitrogen fertilizer management for nitrous oxide (n2o) mitigation in intensive corn (Maize) production: An emissions reduction protocol for US Midwest agriculture. *Mitig. Adapt. Strateg. Glob. Change* **15,** 185–204.

Mills, T. C. (2005). Modelling precipitation trends in England and wales. *Meteorol. Appl.* **12,** 169–176.

Misselbrook, T. H., Webb, J., Chadwick, D. R., Ellis, S., and Pain, B. F. (2001). Gaseous emissions from outdoor concrete yards used by livestock. *Atmos. Environ.* **35,** 5331–5338.

Mohamoud, Y. M., Sigleo, A. C., and Parmar, R. (2009). Modeling the Impacts of Hydromodification on Water Quantity and Quality. National Exposure Research Laboratory Ecosystems Research Division, Athens, GA.

Monteny, G. J., Bannink, A., and Chadwick, D. (2006). Greenhouse gas abatement strategies for animal husbandry. *Agric. Ecosyst. Environ.* **112,** 163–170.

Morgan, R. P. C., Quinton, J. N., Smith, R. E., Govers, G., Poesen, J. W. A., Auerswald, K., Chisci, G., Torri, D., and Styczen, M. E. (1998). The EUROPEAN Soil Erosion Model (EUROSEM): A dynamic approach for predicting sediment transport from fields and small catchments. *Earth Surf. Process. Land.* **23,** 527–544.

Morris, C., and Winter, M. (1999). Integrated farming systems: The third way for European agriculture? *Land Use Policy* **16,** 193–205.

Murray, P. J., Clegg, C. D., Crotty, F. V., Martinez, N. d. l. F., Williams, J. K., and Blackshaw, R. P. (2009). Dissipation of bacterially derived C and N through the meso- and macrofauna of a grassland soil. *Soil Biol. Biochem.* **41,** 1146–1150.

National Environmental Research Institute. (2000). Guideline 8: Principles for source apportionment for quantifying nitrogen and phosphorus discharges and losses. Silkeborg, Denmark.

Nunez, P. A., Demanet, R., Misselbrook, T. H., Alfaro, M., and Mora, M. D. (2010). Nitrogen losses under different cattle grazing frequencies and intensities in a volcanic soil of southern Chile. *Chilean J. Agric. Res.* **70,** 237–250.

Palmer, T. N., and Ralsanen, J. (2002). Quantifying the risk of extreme seasonal precipitation events in a changing climate. *Nature* **415,** 512–514.

Parton, W. J. (1996). Ecosystem model comparison: Science or fantasy world. *In* "Evaluation of Soil Organic Matter Models. NATO ASI Series, Vol. 38" (D. S. Powlson, P. Smith, and J. U. Smith, Eds.), pp. 3–11. Springer-Verlag, Berlin.

Parton, W. J., Schimel, D. S., Cole, C. V., and Ojima, D. S. (1987). Analysis of factors controlling soil organic-matter levels in great-plains grasslands. *Soil Sci. Soc. Am. J.* **51,** 1173–1179.

Parton, W. J., Hartman, M., Ojima, D., and Schimel, D. (1998). DAYCENT and its land surface submodel: Description and testing. *Glob. Planet. Change* **19,** 35–48.

Parton, W. J., Holland, E. A., Del Grosso, S. J., Hartman, M. D., Martin, R. E., Mosier, A. R., Ojima, D. S., and Schimel, D. S. (2001). Generalized model for NOx and N2O emissions from soils. *J. Geophys. Res. Atmos.* **106,** 17403–17419.

Pattey, E., Edwards, G. C., Desjardins, R. L., Pennock, D. J., Smith, W., Grant, B., and MacPherson, J. I. (2007). Tools for quantifying N2O emissions from agroecosystems. *Agric. For. Meteorol.* **142,** 103–119.

Pereira, J., Fangueiro, D., Chadwick, D. R., Misselbrook, T. H., Coutinho, J., and Trindade, H. (2010). Effect of cattle slurry pre-treatment by separation and addition of nitrification inhibitors on gaseous emissions and N dynamics: A laboratory study. *Chemosphere* **79,** 620–627.

Pilgrim, E. S., Macleod, C. J. A., Blackwell, M. S. A., Bol, R., Hogan, D. V., Chadwick, D. R., Cardenas, L., Misselbrook, T. M., Haygarth, P. M., Hobbs, P., Jarvis, S., Hodgson, C., *et al.* (2010). Interactions among agricultural production and other ecosystem services delivered from European Grasslands. *Adv. Agron.* **109,** 117–154.

Pinares-Patino, C. S., D'Hour, P., Jouany, J. P., and Martin, C. (2007). Effects of stocking rate on methane and carbon dioxide emissions from grazing cattle. *Agric. Ecosyst. Environ.* **121,** 30–46.

Ptashnyk, M., Roose, T., and Kirk, G. J. D. (2010). Diffusion of strongly sorbed solutes in soil: A dual-porosity model allowing for slow access to sorption sites and time-dependent sorption reactions. *Eur. J. Soil Sci.* **61,** 108–119.

Ramanathan, V., and Xu, Y. Y. (2010). The Copenhagen Accord for limiting global warming: Criteria, constraints, and available avenues. *Proc. Natl. Acad. Sci. USA* **107,** 8055–8062.

Regina, K., Lehtonen, H., Nousiainen, J., and Esala, M. (2009). Modelled impacts of mitigation measures on greenhouse gas emissions from Finnish agriculture up to 2020. *Agric. Food Sci.* **18,** 477–493.

Richards, L. A. (1931). Capillary conduction of liquids through porous mediums. *Physics* **1,** 318–333.

Riedo, M., Gyalistras, D., and Fuhrer, J. (2000). Net primary production and carbon stocks in differently managed grasslands: Simulation of site-specific sensitivity to an increase in atmospheric CO2 and to climate change. *Ecol. Modell.* **134,** 207–227.

Ritchie, J. T. (1998). Soil water balance and plant water stress. Kluwer Academic Publishers, Dordrecht, Netherlands.

Robertson, G. W. (1968). A biometeorological time scale for a cereal crop involving day and night temperatures and photoperiod. *Int. J. Biometeorol.* **12,** 191–223.

Rubino, M., Dungait, J. A. J., Evershed, R. P., Bertolini, T., De Angelis, P., D'Onofrio, A., Lagomarsino, A., Lubritto, C., Merola, A., Terrasi, F., and Cotrufo, M. F. (2010). Carbon input belowground is the major C flux contributing to leaf litter mass loss: Evidences from a C-13 labelled-leaf litter experiment. *Soil Biol. Biochem.* **42,** 1009–1016.

Ryden, J. C., Ball, P. R., and Garwood, E. A. (1984). Nitrate leaching from grassland. *Nature* **311,** 50–53.

Scholefield, D., Hawkins, J. M. B., and Jackson, S. M. (1997). Use of a flowing helium atmosphere incubation technique to measure the effects of denitrification controls applied to intact cores of a clay soil. *Soil Biol. Biochem.* **29,** 1337–1344.

Schoumans, O. F., and Silgram, M. (2003). Review and literature evaluation of nutrient quantification tools. Rep. No. NIVA report SNO 4739–2003, Oslo, Norway, 120pp.

Shaffer, M. J., and Ma, L. (2001). Carbon and nitrogen modelling in upland soils. *In* "Modelling Carbon and Nitrogen Dynamics for Soil Management" (M. J. Shaffer, L. Ma, and S. Hansen, Eds.), Lewis, Boca Raton.

Shepherd, M. A., Davies, D. B., and Johnson, P. A. (1993). Minimizing nitrate losses from arable soils. *Soil Use Manage.* **9,** 94–99.

Shibu, M. E., Leffelaar, P. A., Van Keulen, H., and Aggarwal, P. K. (2006). Quantitative description of soil organic matter dynamics—A review of approaches with reference to rice-based cropping systems. *Geoderma* **137,** 1–18.

Shih, J., Burtraw, D., Palmer, K., and Siikamaki, J. (2006). Air emissions of ammonia and methane from livestock operations: Valuation and policy options. Discussion Paper—Resources for the Future (RFF), 28 pp.

Slafer, G. A., and Rawson, H. M. (1995). Photoperiod X temperature interactions in contrasting wheat genotypes: Time to heading and final leaf number. *Field Crops Res.* **44,** 73–83.

Smith, J. U., Bradbury, N. J., and Addiscott, T. M. (1996). SUNDIAL: A PC-based system for simulating nitrogen dynamics in arable land. *Agron. J.* **88,** 38–43.

Smith, P., Smith, J. U., Powlson, D. S., McGill, W. B., Arah, J. R. M., Chertov, O. G., Coleman, K., Franko, U., Frolking, S., Jenkinson, D. S., Jensen, L. S., Kelly, R. H., *et al.* (1997). A comparison of the performance of nine soil organic matter models using datasets from seven long-term experiments. *Geoderma* **81,** 153–225.

Smith, J. U., Smith, P., Dailey, A. G., Glendining, M. J., Tuck, G., and Leech, P. (2004). The SUNDIAL Model. Wageningen Academic Publishers, Wageningen.

Smith, J., Foereid, B., Smith, P., and Zhang, C. (2006). Offline Validation of the MAGEC Soil Nitrogen and Carbon Model. Hadley Centre for Climate and Prediction. Rep. No. MS-RAND-CPP-PROG0407.

Stevens, C. J., and Quinton, J. N. (2009a). Diffuse pollution swapping in arable agricultural systems. *Crit. Rev. Environ. Sci. Technol.* **39,** 478–520.

Stevens, C. J., and Quinton, J. N. (2009b). Policy implications of pollution swapping. *Phys. Chem. Earth* **34,** 589–594.

Stromqvist, J., Collins, A. L., Davison, P. S., and Lord, E. I. (2008). PSYCHIC—A process-based model of phosphorus and sediment transfers within agricultural catchments. Part 2. A preliminary evaluation. *J. Hydrol.* **350,** 303–316.

Suntararak, S. (2010). A quantitative analysis of macronutrients in the mixed of food scraps and agricultural waste compost. *In* "Proceedings of the 48th Kasetsart University Annual Conference," Kasetsart UniversityKasetsart, 3–5 March, 2010. Subject: Natural Resources and Environment, pp. unpaginated.

Thorburn, P. J., Biggs, J. S., Collins, K., and Probert, M. E. (2010). Using the APSIM model to estimate nitrous oxide emissions from diverse Australian sugarcane production systems. *Agric. Ecosyst. Environ.* **136,** 343–350.

Thornley, J. H. M., and Verberne, E. L. J. (1989). A model of nitrogen flows in grassland. *Plant Cell Environ.* **12,** 863–886.

Tiktak, A., and Vangrinsven, H. J. M. (1995). Review of 16 forest-soil-atmosphere models. *Ecol. Modell.* **83,** 35–53.

Tilman, D. (1999). Global environmental impacts of agricultural expansion: The need for sustainable and efficient practices. *Proc. Natl. Acad. Sci. USA* **96,** 5995–6000.

Tramblay, Y., Bouvier, C., Martin, C., Didon-Lescot, J. F., Todorovik, D., and Domergue, J. M. (2010). Assessment of initial soil moisture conditions for event-based rainfall-runoff modelling. *J. Hydrol.* **387,** 176–187.

Turner, B. L., and Haygarth, P. M. (2001). Biogeochemistry—Phosphorus solubilization in rewetted soils. *Nature* **411,** 258.

US Department of Agriculture Soil Conservation Service (1972). SCS-National Engineering Handbook. Section 4: Hydrology.

US Environmental Protection Agency (2001). Better Assessment Science Integrating Point and Non-point Sources (BASINS Version 3.1). Office of Water. US Environmental Protection Agency, Washington, DC.

Van Der Meer, H. G. (2008). Optimising manure management for GHG outcomes. *Aust. J. Exp. Agric.* **48,** 38–45.

Van Wesemael, B., Paustian, K., Meersmans, J., Goidts, E., Barancikova, G., and Easter, M. (2010). Agricultural management explains historic changes in regional soil carbon stocks. *Proc. Natl. Acad. Sci. USA* **107,** 14926–14930.

Venohr, M., Behrendt, H., and Kluge, W. (2005). The effects of different input data and their spatial resolution on the results obtained from a conceptual nutrient emissions model: The River Stor case study. *Hydrol. Process.* **19,** 3501–3515.

Verberne, E. L. J., Hassink, J., Dewilligen, P., Groot, J. J. R., and Vanveen, J. A. (1990). Modeling organic-matter dynamics in different soils. *Neth. J. Agric. Sci.* **38,** 221–238.

Vidal, J. P., and Wade, S. D. (2008). Multimodel projections of catchment-scale precipitation regime. *J. Hydrol.* **353,** 143–158.

Wade, A. J., Durand, P., Beaujouan, V., Wessel, W. W., Raat, K. J., Whitehead, P. G., Butterfield, D., Rankinen, K., and Lepisto, A. (2002). A nitrogen model for European catchments: INCA, new model structure and equations. *Hydrol. Earth Syst. Sci.* **6,** 559–582.

WFD-UKTAG (2001). http://www.wfduk.org/. Website documentation of WFD-UKTAG, the United Kingdom Technical Advisory Group (UKTAG) supporting the implementation of the European Community (EC) Water Framework Directive (Directive 2000/60/EC).

Wheeler, D. M., Ledgard, S. F., and DeKlein, C. A. M. (2008). Using the OVERSEER nutrient budget model to estimate on-farm greenhouse gas emissions. *Aust. J. Exp. Agric.* **48,** 99–103.

Whitehead, P. G., Wilson, E. J., and Butterfield, D. (1998). A semi-distributed Integrated Nitrogen model for multiple source assessment in Catchments (INCA): Part I—Model structure and process equations. *Sci. Total Environ.* **210,** 547–558.

Whitmore, A. P. (2007). Describing the transformation of organic carbon and nitrogen in soil using the MOTOR system. *Comput. Electron. Agric.* **55,** 71–88.

Whitmore, A. P., Klein-Gunnewiek, H., Crocker, G. J., Klir, J., Korschens, M., and Poulton, P. R. (1997). Simulating trends in soil organic carbon in long-term experiments using the Verberne/MOTOR model. *Geoderma* **81,** 137–151.

Whittemore, R. C., and Beebe, J. (2000). EPA's basins model: Good science or serendipitous modelling? *J. Am. Water Resour. Assoc.* **36,** 493–499.

Wu, L., McGechan, M. B., McRoberts, N., Baddeley, J. A., and Watson, C. A. (2007). SPACSYS: Integration of a 3D root architecture component to carbon, nitrogen and water cycling-model description. *Ecol. Modell.* **200,** 343–359.

Zhang, Y., Li, C. S., Zhou, X. J., and Moore, B. (2002). A simulation model linking crop growth and soil biogeochemistry for sustainable agriculture. *Ecol. Modell.* **151,** 75–108.

Zhang, C. F., Meng, F. R., Bhatti, J. S., Trofymow, J. A., and Arp, P. A. (2008). Modeling forest leaf-litter decomposition and N mineralization in litterbags, placed across Canada: A 5-model comparison. *Ecol. Modell.* **219,** 342–360.

CHAPTER TWO

Nitrogen Dynamics and Indices to Predict Soil Nitrogen Supply in Humid Temperate Soils

Mervin St. Luce,[*,†] Joann K. Whalen,[*] Noura Ziadi,[†] *and* Bernie J. Zebarth[‡]

Contents

Abstract

Knowledge of the nitrogen (N) available to crops during the growing season is essential for improving fertilizer-use efficiency and minimizing the adverse impacts of N losses on the environment. In humid temperate regions, soil N supply is dominated by in-season N mineralization because plant-available

* Department of Natural Resource Sciences, Macdonald Campus of McGill University, Ste-Anne-de-Bellevue, Quebec, Canada
† Soils and Crops Research and Development Centre, Agriculture and Agri-Food Canada, Quebec City, Quebec, Canada
‡ Potato Research Centre, Agriculture and Agri-Food Canada, Fredericton, New Brunswick, Canada

Advances in Agronomy, Volume 112
ISSN 0065-2113, DOI: 10.1016/B978-0-12-385538-1.00002-0

N (NH_4–N and NO_3–N) is transformed to nonlabile forms or lost from the soil–plant system during fall and winter. The microbially mediated reactions that generate the soil N supply in agroecosystems are affected by system-specific conditions, including soil properties, agricultural management (crop rotation, tillage system, organic amendments), and most importantly, climate. Potentially mineralizable N (N_o) determined from long-term soil incubation is regarded as the standard measure of soil N mineralization potential and may provide a good approximation of the soil N supply. However, this method is time consuming and not practical for routine use. Several chemical methods to estimate the N mineralization potential of soils are discussed in this chapter. The major limitation of chemical methods is that they cannot simulate the microbial-mediated release of plant-available N under field conditions. Consequently, any single chemical method may not be a good predictor of soil N supply. Thus, we suggest a holistic approach to estimate soil N supply in humid temperate regions, which involves (1) the use of a combination of N indices together with weather data and (2) identification and quantification of a specific fraction (s) of organic N that is the dominant contributor (s) to N supply in a particular system.

1. Introduction

Nitrogen (N) is the most limiting nutrient for crop production in humid temperate soils, although the total N content in these soils can be quite appreciable (e.g., 0.48–3.36 g N kg^{-1} in meadow soils in Quebec, Canada; Simard and N'Dayegamiye, 1993). Organic N forms constitute up to 90% of the total N in the plow layer of mineral soils (Olk, 2008b), and only about 1–4% is mineralized as plant-available N (NH_4–N and NO_3–N) each year (Tisdale *et al.*, 1985). Mineralization of organic N is seldom sufficient to achieve the maximum yield possible with modern cultivars, so additional N from mineral fertilizer or organic sources (e.g., animal manures and legume residues) is needed. Plant-available N released from soil organic N (SON) or applied in fertilizer is highly susceptible to loss from the soil–plant system through leaching and denitrification. This means that N management is of great importance for both economic and environmental reasons. Optimizing N management will improve agronomic performance and increase economic returns, as well as reduce N losses to the environment. One approach to reduce environmental pollution and improve profitability is to tailor fertilizer N applications to meet N crop requirement (Sharifi *et al.*, 2007a; Zebarth and Rosen, 2007) by synchronizing the application of plant-available N with crop N uptake in space and time (Ma *et al.*, 1999). However, this is difficult to achieve due to substantial variation in both crop N demand and in soil N supply across years and within and between fields (Zebarth *et al.*, 2009). In arid and semi-arid environments, soil N supply consists of mineralization of SON, crop

residues, and other organic amendments plus residual soil mineral N from the previous growing season. However, in humid temperate regions, N supply consists primarily of in-season N mineralization due to significant N losses during fall and winter (Zebarth *et al.*, 2009). Although considerable progress has been made in understanding the controls of N availability in crop production systems, we still do not have a soil N test that can reliably predict the N supply in humid temperate regions.

This chapter discusses soil N dynamics, current measures for estimating soil N supply, and suggests a holistic approach to predicting N availability in cropland of humid temperate regions.

2. Nitrogen Dynamics

2.1. Importance of nitrogen in crop production

Nitrogen occupies a unique position among essential elements because agricultural crops require proportionally more N than other nutrients to achieve maximum yield. For instance, fertilizer recommendations in Quebec, Canada are 120–170 kg N ha^{-1} and 20–95 kg P_2O_5 ha^{-1} for corn (*Zea mays* L.), and 40–120 kg N ha^{-1}, 20–80 kg P_2O_5 ha^{-1}, and 20–90 kg K_2O ha^{-1} for wheat (*Triticum aestivum* L.; Centre de référence en agriculture et agroalimentaire du Québec, 2003). Nitrogen is considered the most important growth-limiting factor in nonlegumes (cereal crops; Zebarth *et al.*, 2009). Plants that have not received sufficient N exhibit stunted growth and gradual leaf yellowing but respond quickly to N inputs (e.g., leaves turn deep green in color due to the central role of N in chlorophyll synthesis). As few soils supply enough N to sustain satisfactory crop production without fertilizer, N deficiency is more widespread than any other nutrient deficiency in crops.

Rapid increases in crop yields became possible with the introduction of mineral N fertilizers. The positive effect of mineral N fertilizer application on yield is well documented for crops grown in humid temperate regions, such as potato (*Solanum tuberosum* L.; Bélanger *et al.*, 2000; Zebarth and Rosen, 2007; Ziadi *et al.*, 2011), wheat (Holford and Doyle, 1992; Westerman *et al.*, 1994), barley (*Hordeum vulgare* L.; Zebarth *et al.*, 2008), corn (Gagnon and Ziadi, 2010; Halvorson and Reule, 2006; Stanger and Lauer, 2008), and forage grasses (Ziadi *et al.*, 2000). Fertilizer N contribution to total N inputs into agricultural systems rose from just 7% in 1950 to 43% by 1996 (Mosier, 2001) and should continue to increase, especially in areas where the arable land base is shrinking and the goal is to increase output per unit area through more intensive agricultural management (Mosier, 2001). Improvement of N-use efficiency from fertilizer is critical since the average recovery of added N is about 50% globally (Smil, 1999) and overapplication

of fertilizer can result in N losses from the soil–plant system that affect surface and groundwater resources (Fageria and Baligar, 2005).

2.2. The global nitrogen cycle

The global N cycle (Fig. 1) describes the principal pools and forms of N, and the processes by which N is transformed in terrestrial ecosystems. Nitrogen exists in the atmosphere as dinitrogen gas (N_2), oxides (N_2O, NO, and NO_2), and in the reduced form (NH_3). These N forms also exist in soil water as dissolved gases. Hart *et al.* (1994) explained that the biogeochemical cycling of N in terrestrial ecosystems can be divided into an external and internal cycle. The external cycle includes processes that add N to ecosystems (N_2 fixation, ammonium (NH_4^+) and nitrate (NO_3^-) in rainwater, mineral and organic N fertilizer applications) and cause N loss from ecosystems (denitrification, NO_3^- leaching, and NH_3 volatilization). In contrast, the internal N cycle consists of processes that convert N from one chemical form to another or transfer N between ecosystem pools including plant assimilation, return of N to the soil in plant litter-fall and root turnover, N mineralization, and microbial immobilization. The entrance, removal

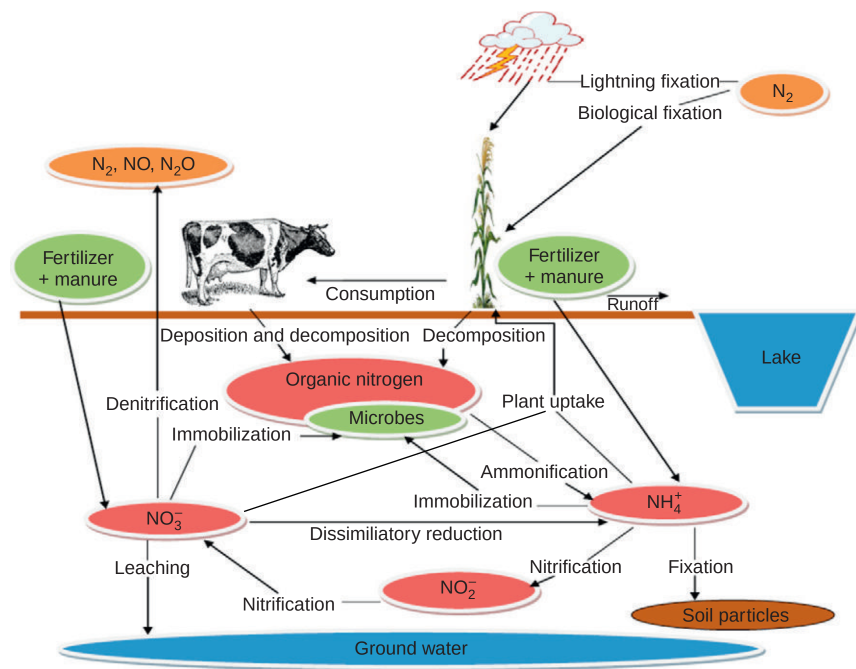


Figure 1 Illustration of the nitrogen cycle in soil.

and/or lost and subsequent reentry of N between the soil and atmosphere complete the global N cycle.

2.3. Nitrogen cycling in the plant–soil system

Nitrogen cycling in the soil–plant system is very complex and involves interactions between soil and plant factors. The major N transformation processes in this system in humid temperate soils are mineralization, nitrification, immobilization (refer to Section 2.5.1), and denitrification (refer to Section 2.6.1). The mineralization of organic N compounds into inorganic N (considered the major source of plant-available N) generates the soil N supply; it is also an important starting point for potential losses of N and attendant adverse environmental impacts (Myrold and Bottomley, 2008). Mineralization occurs largely through biological activities that are temperature and moisture dependent (Agehara and Warncke, 2005; Stevenson, 1986). Recently, Kemmitt *et al.* (2008) suggested that N mineralization is not regulated by the size, composition, or activity of the soil microbial biomass, rather, an abiological process termed the "regulatory gate" controls the rate-limiting step of N mineralization. This has triggered an interesting debate among researchers (Brookes *et al.*, 2009; Kuzyakov *et al.*, 2009).

The N mineralization process consists of sequential aminization and ammonification reactions. Aminization requires extracellular enzymes of bacterial and fungal origin such as proteinases and proteases that break down complex proteins into simpler amino acids and amino sugars (Myrold, 2005; Whalen and Sampedro, 2010). These small organic N compounds are further hydrolyzed within microbial cells by intracellular enzymes such as arylamidase and amidohydrolase during ammonification to yield NH_4^+. The amine (NH_2–CR_3) and amide (NH_2–CR=O) functional groups are two N forms in amino acids that undergo degradation. Amide groups are cleaved by specific enzymes, for instance, asparagine and glutamine are hydrolyzed by asparaginase and glutaminase. Amino-N is released by amino acid dehydrogenases and amino acid oxidases by deamination (Myrold, 2005). Amino sugars are metabolized in two steps. They are phosphorylated by a kinase, and then NH_4^+ is released through deamination (Myrold, 2005; Whalen and Sampedro, 2010).

Humid temperate soils often have low NH_4^+ concentration because it is rapidly converted into NO_3^- through nitrification by chemoautotrophic microorganisms (Whalen and Sampedro, 2010). This reaction often limits the amount of NH_4^+ available for plant uptake following the application of NH_4-based fertilizers (Subbarao *et al.*, 2006). However, the nitrification rate can be reduced by banding of NH_4-based fertilizers due to high osmostic pressure or high pH in the bands (Malhi and Nyborg, 1988; Wetselaar *et al.*, 1972) and toxicity of high NH_3 concentration (Malhi and McGill, 1982). Nitrification involves three key reactions. Ammonium is first oxidized to

hydroxylamine and then to nitrite (NO_2^-) by ammonia-oxidizing bacteria (AOB) and archaea (AOA), and finally to NO_3^- by nitrite-oxidizing bacteria (Whalen and Sampedro, 2010). The advent of advanced molecular techniques such as quantitative real-time polymerase chain reaction (qRT-PCR) and stable isotope probing has recently illustrated the importance of AOA in soil (Gleeson *et al.*, 2010; Nicol *et al.*, 2008; Treusch *et al.*, 2005). The AOB (*Nitrosomonas* being the most well known) use hydroxylamine oxidoreductase to transform hydroxylamine to NO_2^-. Some AOB also denitrify the NO_2^- to NO, N_2O, and N_2 through the nitrifier–denitrification pathway (Wrage *et al.*, 2001), and therefore cause gaseous N loss from the soil–plant system. Nitrite does not accumulate in soil because it is rapidly transformed to NO_3^- by nitrifiers (*Nitrobacter* being the most well known) that possess nitrite oxidoreductase or other oxidizing enzymes (Whalen and Sampedro, 2010). Heterotrophic microorganisms including fungi (e.g., *Aspergillus*) and bacteria (e.g., *Alcaligenes* and *Arthrobacter* spp.) can also oxidize either NH_4^+ or organic N to NO_2^- or NO_3^- (Myrold, 2005). In addition, other microbes can produce NO_2^- and NO_3^- by enzymatic oxidations that are not linked to microbial growth (Myrold, 2005; Sahrawat, 2008; Whalen and Sampedro, 2010).

2.4. Soil nitrogen supply in humid temperate soils

While biological N_2 fixation makes an important contribution to the N requirements of leguminous crops (about 40–60%; Herridge *et al.*, 2008), nonleguminous crops must absorb plant-available N from the soil, mainly NH_4^+ and NO_3^- from mineralization and nitrification reactions, as well as free amino acids (Adamczyk *et al.*, 2010; Jones *et al.*, 2005; Sauheitl *et al.*, 2009). Plant-available NH_4–N must be distinguished from fixed NH_4–N bound within the expanding lattices of clay minerals that is either sparingly available or unavailable for plant uptake. Chantigny *et al.* (2004) showed that clayey soils in the humid regions of Eastern Canada were a sink for NH_4–N as up to 34% of recently added NH_4-based fertilizers were fixed in the clay fraction.

In humid temperate regions, most of the plant-available N remaining from the previous growing season is lost from the rooting zone during fall and winter due to high soil moisture. Therefore, soil N supply in these conditions is controlled by mineralization of SON during the growing season (Zebarth *et al.*, 2005, 2009). In some instances, N supplied from SON may exceed the N absorbed from mineral fertilizers. A study with ^{15}N-labeled fertilizer showed that current-year N fertilization contributed only 10–50% of the total N uptake by corn, with the remainder supplied from soil N (Stevens *et al.*, 2005). Wu *et al.* (2008) reported that 87% of the N uptake by corn in Ontario came from N mineralization and nitrification.

2.5. Factors affecting nitrogen supply in humid temperate soils

According to Zebarth *et al.* (2009), N supply is sensitive to the factors that control N mineralization potential (e.g., soil properties and agricultural management) and to environmental conditions (e.g., moisture and temperature) that regulate the biological activity controlling the mineralization process. Hence, soil chemical, physical, and biotic properties, and agricultural practices that affect the concentration and biochemical degradation of SON will affect the soil N supply.

2.5.1. Soil chemical properties

Soil chemical properties including pH, electrical conductivity (EC), cation exchange capacity (CEC), C/N ratio of added amendment, and organic matter (OM) content can impact soil N supply (Dharmakeerthi *et al.*, 2005; Subbarao *et al.*, 2006) by influencing the activity of microorganisms and the concentrations of NH_4^+ and NO_3^- in the soil solution. Many soil microorganisms function optimally in the soil microenvironment with a pH ranging from 6 to 7 since most soil nutrients are available in this range (Hartel, 2005); however, this depends on the microbial group, given that the activity of N-mineralizing bacteria is greatest between pH 6.5 and 8, whereas pH 5.5–6.5 is ideal for fungi (Whalen and Sampedro, 2010). Soil microorganisms responsible for N mineralization are less sensitive to increases in soil pH and EC than nitrifier populations (Griffin, 2008). Thus, nitrification is rapid in soils with a pH $\geq$ 6.0 but slower in soils with a pH $\leq$ 5.0 (Sahrawat, 2008; Subbarao *et al.*, 2006). In a 15-day incubation experiment with various soils treated with 100 ppm of NH_4^+–N as $(NH_4)_2SO_4$, Dancer *et al.* (1973) found a three- to fivefold increase in nitrification as soil pH increased from 4.7 to 6.5. De Neve *et al.*(2003) incubated a loamy sand for 173 days at six different temperatures (5.5–30 °C) and at a constant water content (80%) and reported that the EC of the soil extracts increased significantly with increasing temperature, and was strongly correlated ($r = 0.96$) to N mineralization. Pathak and Rao (1998) measured NH_4–N up to EC 70 dSm^{-1}, while NO_3–N was undetectable at EC < 26 dSm^{-1} in saline and sodic soils. They concluded that net N mineralization decreased with increasing pH or salinity. The CEC of a soil represents its ability to store and release cations such as NH_4^+ into the soil solution for plant uptake. This significantly reduces the potential leaching losses of plant-available N, thus enhancing the N supply capability of the soil. In a 6-week greenhouse experiment involving 21 soils, Abadín *et al.*(2010) reported that mineralized N and N uptake by wheat were significantly correlated to CEC ($r = 0.68$ and 0.60, respectively).

Crop residue quality, related to lignin content and C/N ratio, determines whether microorganisms will immobilize mineral N or release it into

the soil solution, as low N concentration in soil solution limits microbial growth (Henriksen and Breland, 1999). Soil N supply is greatly reduced during the early stages of decomposition of plant residues with high C/N ratios because of the greater N demand by the microbial biomass in response to the input of available carbon (C). Hence, net immobilization occurs when microorganisms assimilate recently mineralized N and inorganic N from the soil solution. Green *et al.* (1995) showed that rapid immobilization of mineral N occurs during the initial decomposition of corn stover. However, as decomposition proceeds, the C/N ratio of the residue becomes lower and the activity and population of soil microbes is reduced due to limited C availability, resulting in the release of mineral N from the both the decomposing residue and dead microbes. It is well known that soils amended with organic materials having a C/N ratio less than 20:1 generally exhibit net mineralization. The C/N ratio of the microbial population is also critical. The C/N ratio of microorganisms can range from 4 to 5 for bacteria, and to as high as 15 for fungi (Myrold, 2005). As fungal biomass contains more C per unit N than bacterial biomass, fungal activity is more likely to stimulate mineralization, although this depends on substrate quality and environmental conditions.

Soils with higher OM content are expected to have larger microbial populations and activity. Schnürer *et al.* (1985) reported significant correlations between microbial biomass and activity and SOM. Also, soils with a higher OM content, especially due to manure applications, typically have a greater N mineralization potential (Sharifi *et al.*, 2008b). Delin and Lindén (2002) found that N mineralization was controlled by OM and clay content. Soil OM is a heterogeneous mixture of organic compounds with variable molecular weights and physical locations in the soil (e.g., in the soil solution, adsorbed onto clay minerals, on the external or internal surfaces of aggregates). Consequently, the turnover of these molecules may range from days to millenia (Kleber, 2010). The labile fractions in soil OM containing N are of greatest relevance to this discussion since they are expected to rapidly cycle through the mineralization–immobilization reactions that control the supply of plant-available N (Duxbury *et al.*, 1991; Gregorich *et al.*, 1994; Haynes, 2005).

2.5.2. Soil physical properties

Soil physical characteristics such as texture exert a considerable influence on soil moisture content, porosity, and the habitat present for microbes responsible for N mineralization and nitrification, thus impacting soil N supply (Griffin, 2008; Subbarao *et al.*, 2006). The N mineralization rate is generally greater in sandy soils than in silt or clay soils due to better aeration and less physical protection of labile OM (Griffin, 2008; Sahrawat, 2008). However, sandy soils are more susceptible to N loss through leaching, which can affect the synchrony between N supply and crop N demand.

In this chapter, soil moisture and temperature are considered among the soil physical characteristics controlling soil N supply because these parameters affect microbial activity and biochemical processes in the soil. Soil moisture and temperature also influence the solubility and movement of plant-available N in the soil solution to plant roots, and the potential N loss pathways such as leaching and denitrification. Kolberg *et al.* (1999) stated that changes in both soil moisture and temperature have a greater effect on N mineralization than their individual additive effects alone. While the response of N mineralization to soil moisture varies with temperature, the spatial variability in soil water content is expected to be greater than the variability in soil temperature during the period of greatest crop N demand (Drury *et al.*, 2003). Whalen *et al.* (2001) aerobically incubated clay–loam soils collected from long-term manured plots in Alberta, Canada for 20 weeks under four different combinations of soil temperature (10 and 20 °C) and moisture (50% and 75% of field capacity (FC)) and reported higher microbial activity and greater N mineralization in hotter, wetter soils than colder, drier soils. Although mineralization did not double in response to a 10 °C increase in temperature (Q_{10}), soils incubated at 50% of FC exhibited greater Q_{10} values than soils incubated at 75% of FC. This suggests that the temperature influence on N mineralization is greater in oxic soils than those approaching anoxic conditions.

Temperature directly controls N mineralization by affecting biochemical processes and, indirectly, by affecting oxygen (O_2) consumption by microorganisms and the aerobic volume of the soil (Sierra, 1997). Mineralization rates increased linearly in five Queensland soils as temperature increased to 40 °C (Campbell *et al.*, 1981). Griffin and Honeycutt (2000) incubated various types of livestock manure for 112 days at 10, 17, and 24 °C and reported that the rate of nitrification increased linearly with increasing temperature. Stanford *et al.* (1973) noted that while ammonification continues above 35 °C, nitrification ceases at 45 °C. Temperatures between 25 and 35 °C are regarded as optimal for aerobic microorgnisms (Whalen and Sampedro, 2010), yet microbial activity and organic residue decomposition continue when temperatures fall below freezing (Breland, 1994).

Soil moisture content between 50% and 80% FC is regarded as optimal for N mineralization (Whalen and Sampedro, 2010). Soil moisture content regulates O_2 diffusion for maximum aerobic microbial activity and enhances microbial mobility and diffusion of soluble substrates to microbes (Agehara and Warncke, 2005). In dry soils, reduced O_2 and substrate diffusion coupled with reduced microbial mobility and growth decreases microbial activity and N mineralization. In very wet soils, reduced activity and mobility of aerobic microbes is attributed to O_2 deprivation resulting from slow diffusion (Paul *et al.*, 2003). Nitrogen mineralization rate generally increases with soil moisture up to 60% water-field pore space (De Neve and Hofman, 2002). Agehara and Warncke (2005) reported net mineralized

N values from SOM of 6.9, 9.9, and 11.3 mg N kg^{-1} at 50%, 70%, and 90% water-holding capacity, respectively after 12 weeks of incubation.

While many studies are done under constant temperature and moisture regimes, fluctuating soil temperature and moisture conditions are more realistic. Haynes (1986) suggested that fluctuating temperatures may inhibit microbial activity; however, Sierra (2002) reported similar microbial activity under fluctuating temperature as under constant temperature, when the same average temperature conditions were considered. Greater N mineralization in two fluctuating temperature patterns (FTP; FTP1: 8 h at 20 °C, 8 h at 30 °C, and 8 h at 40 °C; FTP2: 12 h at 20 °C and 12 h at 40 °C) than at a constant of 30 °C in an Oxisol was reported by Sierra (2002), while Stanford *et al.* (1975) found no effect on N mineralization of fluctuating temperatures between 5 and 35 °C in three soils incubated for 52 days. Miller *et al.* (2005) found greater net mineralization and nitrification in chaparral soils with repeated rewetting. However, Mikha *et al.* (2005) reported reduced microbial activity and cumulative N mineralization when soil was repeatedly rewetted, although a flush of mineralized C was observed after each rewetting period. Soil rewetting often causes a flush of N mineralization as microorganisms and other food-web organisms regain activity (Griffin, 2008), but the results of Mikha *et al.*(2005) suggested that rapid N immobilization occurred in response to the increase in easily accessible C after rewetting due to greater microbial activity and/or rapid growth in microbial biomass. As the soil was kept structurally intact throughout their experiment, most of the native SOM was protected from microorganisms.

2.5.3. Soil biotic properties

Interactions between soil animals and microorganisms influence the soil N supply. Grazing of soil microorganisms by soil animals such as protozoa and nematodes liberates plant-available N because the contents of the lysed microbial cells are not completely ingested or assimilated by soil animals. Grazing activities of protozoa and nematodes are influenced by soil moisture and temperature since these organisms live and move through water films (Savin *et al.*, 2001). About 30% of annual net N mineralization in soils is attributed to the activity of grazing animals (Myrold, 2005). Earthworms affect soil N supply through their feeding and casting activities, which forms middens, burrows, and casts. Subler and Kirsch (1998) reported higher concentrations of NH_4–N and dissolved organic N in middens than in bulk soil due to accelerated decomposition and mineralization. Savin *et al.* (2004) noted that earthworm burrowing accelerates N mineralization by changing the soil pore structure, resulting in increased aeration and water infiltration.

Interactions of populations within groups of soil organisms also affect soil N supply. Postma-Blaauw *et al.* (2005) showed that a contramensal

interaction between two nematode species (*Bursilla monhystera* and *Plectus parvus*) increased bacterial biomass and N mineralization in a humid podzol. In pots with different earthworms, Postma-Blaauw *et al.* (2006) showed more immobilization of mineral N into bacterial biomass with *Lumbricus rubellus* and *Lumbricus terrestris* together and *L. rubellus—Apporrectodea caliginosa tuberculata* mixture. However, the interaction between *A. caliginosa tuberculata* and *L. terrestris* increased bacterial growth rate and mineralization of soil C.

Biotic interactions in the rhizosphere have a profound effect on soil N supply. Higher microbial biomass and activity in the rhizosphere than the bulk soil is a well known phenomenon attributed to root-derived organic compounds known as root exudates or rhizodeposits (Mahmood *et al.*, 2005; Nannipieri *et al.*, 2008). Chantigny *et al.* (1996) studied the effect of different plant species (faba beans, alfalfa, timothy, bromegrass, reed canarygrass, and wheat) on microbial biomass in two contrasting soils and found that the differences in microbial biomass C (MBC) were significantly related to rhizodeposit C concentration under each plant species. Some studies have related increased microbial activity to increased N mineralization and potential soil N supply (Hassink *et al.*, 1993; Laungani and Knops, 2009; Puri and Ashman, 1998). Certain microbial species (e.g., *Bacillus*, *Azotobacter*, *Azospirillum*, and *Pseudomonas*) or functional groups associate preferentially with specific types of rhizodeposits and plant residues, and therefore can affect N mineralization (Singh *et al.*, 2004, 2009). Song *et al.* (2007) used *16S rRNA* genes and denaturing gradient gel electrophoresis (DGGE) to analyze the AOB community composition in contrasting cropping systems. They measured significantly higher AOB in a cereal/legume intercropping system (faba beans/corn and faba beans/wheat) than in a monocropped or cereal/cereal intercropping system. Marschner *et al.* (2001) examined Eubacterial community structures in the plant rhizosphere with the same method and reported that plant species, root zone, and soil type as well as their interactions had significant effects on community structure.

2.5.4. Agricultural management

Agricultural management practices such as crop rotation, tillage, and addition of organic and inorganic amendments impact N mineralization and soil N supply through their effects on SON pool, microbial activity, and soil aggregation (Sharifi *et al.*, 2008a; Tan *et al.*, 2007). Deng and Tabatabai (2000) and Ekenler and Tabatabai (2002) reported greater N mineralization and β-glucosaminidase activity in corn, oats (*Avena sativa* L.), and alfalfa (*Medicago sativa* L.) rotations than continuous corn since crop rotations provide a greater diversity of organic materials (rhizodeposits and crop residues), thus enhancing microbial diversity, biomass, and activity. Kolberg *et al.* (1999) reported significantly higher net N mineralization in a wheat-fallow than in a wheat–corn-fallow soil; greater crop residue inputs in the wheat-corn-fallow system appeared to induce immobilization.

Soil N supply is usually enhanced when N-fixing legumes are included in the crop rotation. The response of corn to monoculture (C–C), 2-year rotation (C–S) with soybean [*Glycine max* (L.) Merr.], and 4-year rotation (C–S–W/A–A) with soybean, wheat, and alfalfa under different N input levels was evaluated by Riedell *et al.* (2009). They reported greater NO_3–N levels in soils under C–S–W/A–A across all N input levels than in the other rotations. Deep-rooted legumes like alfalfa scavenge deep residual soil N and increase N availability to subsequent shallow-rooted crops like corn and potato (Sharifi *et al.*, 2008b). Moreover, legumes are known to biological fix N_2, thereby, providing additional N to the system. Up to 150 kg N ha^{-1} yr^{-1} can be biologically fixed by legumes depending on year and legume species (Mueller and Thorup-Kristensen, 2001). This may account for almost 50% of total N used in agriculture (Graham, 2005). There is no doubt that legume crops can increase soil N supply, but their impacts vary widely across years and soil types, and among legume species due to differences in N_2 fixation capacity, rooting patterns, plant biomass, C/N ratio, and crop management (Chantigny *et al.*, 1996; Stark and Porter, 2005; Thorup-Kristensen *et al.*, 2003; Zebarth and Rosen, 2007). Liang *et al.* (2007a,b) reported that the addition of plant residues can significantly increase amino sugar concentration in soils, but the relative increase varied according to the plant nutrient composition and quality. The contribution of the rotation crop to soil N supply is therefore dependent on its ease of decomposition, related to the C/N ratio, NO_3–N and water-soluble compounds released from crop residue (Sharifi *et al.*, 2009c; Thorup-Kristensen *et al.*, 2003). Crop residues with a low C/N ratio are expected to decompose rapidly and cause little immobilization, thereby potentially increasing soil N supply during the early part of the growing season (Willson *et al.*, 2001). Although legumes and other crop residues with lower C/N ratios have high N mineralization potential (Sanchez *et al.*, 2004), the actual soil N supply depends on the subsequent crop species, tillage practices, soil properties, and environmental conditions (Sharifi *et al.*, 2009c; Thorup-Kristensen *et al.*, 2003).

Tillage systems affect N supply by altering soil aggregates and microbial habitats, thus affecting the access of microorganisms to labile SON compounds that can be degraded and contribute to the soil N supply. Conventional tillage systems disrupt soil structural units thereby reducing aggregation, increasing O_2 diffusion, and exposing physically protected OM to microbial attack resulting in faster turnover rates (Mikha and Rice, 2004). Also, incorporation of crop residues and animal manures in conventional tillage systems fosters better contact with the soil, resulting in faster turnover rates (Six *et al.*, 1999). Conversely, no-till systems enhance soil aggregation, and the formation and stabilization of microaggregates within macroaggregates thereby increasing the protection of OM resulting in slower turnover rates of macroaggregates (Six *et al.*, 1999). Some studies have reported greater soil microbial and enzyme activity in no-till systems due to greater soil moisture and retention of residues at the soil surface

(Acosta and Tabatabai, 2001; Deng and Tabatabai, 1996), as well as greater microbial biomass and mineralizable N (Halpern *et al*., 2010; Sharifi *et al*., 2008a), and greater N transformation rates (Muruganandam *et al*., 2010). Additionally, Muruganandam *et al*. (2009) reported that no-till systems enhance N-mineralizing enzyme activities by increasing the proportion of fungi in the microbial community. In Eastern Canada, Simard *et al*. (1994) measured higher mineralizable N and a greater N mineralization rate in minimum tilled than in moldboard plowed soils.

Application of mineral and organic fertilizers can also stimulate microbial growth and activity, increase N mineralization, and soil N supply. Liang and MacKenzie (1996) reported increased microbial biomass N (MBN) due to increased mineral N fertilization in two contrasting soils in Quebec, Canada. Mikha *et al*. (2006) reported that a combination of no-tillage and manure significantly increased N mineralization and sustained soil N supply for 6 years after N application was discontinued. After 13 years of receiving solid beef (*Bos Taurus*) manure, a loam soil in Maine, USA had a significantly greater mineralizable N pool than its nonamended counterpart (Sharifi *et al*., 2008b). Hu and Cao (2007) reported higher MBC, microbial respiration rate, and enzyme activity in compost-treated plots than inorganic fertilizer plots and untreated plots planted with winter wheat and corn. Khorsandi and Nourbakhsh (2007) found that cow manure applied at 100 mg ha^{-1} yr^{-1} for five consecutive years increased the activity of urease by 47%, L-asparaginase by 70%, L-glutaminase by 60%, and β-glucosidase by 78%.

2.6. Pathways of nitrogen loss from humid temperate soils

Nitrogen in humid temperate soils is subject to two major loss pathways: denitrification and leaching. About 40% of all soluble N entering agroecosystems in Canada is lost via leaching and denitrification (Janzen *et al*., 2003). While NH_3 volatilization is also important, the incorporation of mineral and organic N sources has significantly reduced NH_3 volatilization from the soil (Janzen *et al*., 2003; Rochette *et al*., 2009). Nitrogen lost from the soil–plant system significantly reduces the plant-available N concentration, thus negatively impacting soil N supply. The form and concentration of plant-available N, soil texture and moisture, and agricultural management play major roles in defining N loss.

2.6.1. Denitrification

Denitrification is the biochemical reduction of NO_3^- or NO_2^- to gaseous N, either as molecular N or as an oxide of N under anaerobic conditions. This process involves the utilization of NO_3^- as an alternative electron acceptor for O_2 by facultative anaerobes resulting in the reduction of NO_3^- to NO_2^-, which is then subsequently reduced to NO by nitric oxide reductase, N_2O by nitrous oxide reductase and release dinitrogen gas (N_2)

as the end product (Whalen and Sampedro, 2010). Denitrification rates are highly variable (Burton and Beauchamp, 1984) and depend on environmental, soil, and agricultural management factors (Beauchamp, 1997). Dinitrogen gas represents the dominant end-product of denitrification under completely anaerobic conditions, with N_2O being dominant under partially anaerobic conditions (Drury *et al.*, 1992; Richardson *et al.*, 2009), depending on NO_3 and C availability, and soil pH (Davis *et al.*, 2008; Miller *et al.*, 2008). Moreover, the dominant form of gas emitted during denitrification is also influenced by the N_2O molar ratio (N_2O:($N_2 + N_2O$)) (Dambreville *et al.*, 2008; Mosier, 1998; Williams *et al.*, 1998) which varies in space and time (Miller *et al.*, 2008) and regulated by several environmental factors such as moisture content, temperature, redox potential, soil pH, and nitrogen oxide concentrations (Firestone and Davidson, 1989). In humid temperate regions, from 30% to 90% of annual emissions occur during the spring thaw period (Smith *et al.*, 2004; Wagner-Riddle *et al.*, 2007) due to the anoxic conditions in the soil induced by precipitation and snow melt (Teepe *et al.*, 2001) and increased diversity of active denitrifiers (Dunfield and Wagner-Riddle, 2010).

The effect of tillage on denitrification is somewhat ambiguous. Denitrification losses were found to be greater in no-till than tilled systems (Almaraz *et al.*, 2009; Baggs *et al.*, 2003; Gregorich *et al.*, 2005, 2006b, 2007, 2008; Helgason *et al.*, 2005; Tan *et al.*, 2009), which was attributed to higher soil moisture content in no-till systems. Conversely, some studies have reported greater losses in tilled soils compared to no-till (Chatskikh and Olesen, 2007; Drury *et al.*, 2006; Kaharabata *et al.*, 2003), while some reported no differences (Elmi *et al.*, 2003; Petersen *et al.*, 2008; Sey *et al.*, 2008). These ambiguous results are due to differences in annual precipitation, soil texture, and depth of tillage.

Fertilizer N and manure application contribute to denitrification by increasing NO_3–N and C availability. In eastern Quebec, an increase in N fertilization of corn from 120 to 180 kg N ha^{-1} resulted in 40–130% greater denitrification, and 50–200% higher N_2O emission (Chantigny *et al.*, 1998). Denitrification was greater in manure-treated than fertilizer N-treated plots (Chang *et al.*, 1998; Paul and Zebarth, 1997a; Rochette *et al.*, 2000), primarily due to increased C availability (Rochette *et al.*, 2000; Velthof *et al.*, 2003). Manures enhance denitrification by increasing the soil NO_3–N content, supplying the soluble C that serves as the electron donor in the denitrification process, and increasing microbial activity that eventually depletes the soil O_2 concentration (Helgason *et al.*, 2005; Sey *et al.*, 2008). Interestingly, the method of placement of both mineral and organic N sources can be seen as a 'trade off'; fertilizer incorporation reduces NH_3 volatilization, but increases the risk for denitrification in humid conditions (Janzen *et al.*, 2003; Webb *et al.*, 2010). Split applications of N fertilizer can

reduce denitrification (Burton *et al.*, 2008) depending on climatic conditions. Since denitrification is a microbial process, higher rates are expected at higher temperatures (Chirinda *et al.*, 2010; Pelletier *et al.*, 1999); however, denitrification still occurs at subzero temperatures (Phillips, 2007, 2008; Singurindy *et al.*, 2009).

2.6.2. Nitrate leaching

Nitrate leaching is the most important pathway of N loss from the soil–plant system in humid regions because of high soil moisture from annual precipitation and snowmelt, high mobility of NO_3^-, and generally higher NO_3^- than NH_4^+ concentrations in the soil solution (Myrold, 2005; Whalen and Sampedro, 2010). De Jong *et al.*(2007) developed an agro-environmental indicator to monitor potential water pollution through N leaching in Canada, and predicted an average N loss of >20 kg N ha^{-1} in the humid temperate regions. Nitrate leaching is influenced by the interaction of several factors including cropping system, tillage practices, inorganic and organic N management, soil structure, amount of water infiltration, as well as timing of the infiltration event, and poses an environmental risk since NO_3^- that is leached can eventually enter ground and surface waters leading to reduced fresh water quality and eutrophication of aquatic systems. The risk of NO_3–N leaching is generally higher in shallow-rooted crops that have low N recoveries, particularly when grown on coarse-textured soils and receive large inputs of N fertilizer, for example, potato and corn. Zebarth and Rosen (2007) noted that NO_3–N leaching represents the primary form of N loss in potato production. Low residual NO_3–N under irrigated potatoes in eastern Canada was attributed to increased NO_3–N leaching during the growing season (Bélanger *et al.*, 2003). Cumulative NO_3–N loss through tile drainage from a clay–loam soil in southwestern Ontario after 3 years was 82 kg N ha^{-1} for fertilized continuous corn, 100 kg N ha^{-1} for fertilized rotation corn (corn–oat–alfalfa–alfalfa), and 70 kg N ha^{-1} for second year fertilized alfalfa (Tan *et al.*, 2002b). Soil NO_3–N concentration measured at 30 cm depth in spring from 228 commercial potato fields in New Brunswick was 3–100% of soil NO_3–N at harvest in the preceding fall indicating that significant leaching occurs between growing seasons (Zebarth *et al.*, 2003).

Tillage has a variable impact on NO_3–N leaching. Some studies reported greater NO_3–N leaching in no-till systems compared to conventional tillage systems (Patni *et al.*, 1998; Tan *et al.*, 2002a) due to formation of continuous soil macropores that increase NO_3–N movement through preferential flow. Conversely, others have reported greater NO_3–N leaching in conventional tillage partly due to higher rates of denitrification in no-till soils (Mkhabela *et al.*, 2008), greater infiltration in tilled soils (Drury *et al.*, 1993), or enhanced N mineralization in tilled soils (Constantin *et al.*, 2010), while some reported no differences (Fuller *et al.*, 2010; Stoddard *et al.*, 2005).

Tan *et al.* (2002a) measured 83 kg N ha^{-1} in tile drainage water from a no-till site and 64 kg N ha^{-1} from a conventional tillage site over a 5-year period. They attributed their results to improved wet aggregate stability, increased near-surface hydraulic conductivity, and larger earthworm populations that created continuous soil macropores in the no-till site. The effect of tillage on NO_3–N leaching will therefore differ from year to year and between spatial units.

Nitrate leaching generally increases with N fertilizer application rates. However, the timing of N application, particularly manure, coupled with the use of controlled-release N fertilizers can significantly reduce NO_3–N leaching (Fuller *et al.*, 2010; Wilson *et al.*, 2010; Ziadi *et al.*, 2011). The use of cover crops over winter can also reduce NO_3–N leaching. Hooker *et al.* (2008) reported that the use of a cover crop (mustard (*Sinapsis alba*)) over winter reduced NO_3–N leaching from spring barley (*Hordeum vulgare* L.) by 38–70%. Further reductions in NO_3–N leaching losses can be achieved through improvements in N-use efficiency by synchronizing N inputs to crop N demand and efficient use of irrigation water (Zebarth *et al.*, 2009).

Although N losses through denitrification (Paul and Zebarth, 1997a) and leaching (Drury *et al.*, 1996) are problematic when they occur outside the growing season, these processes can also occur when crops are present. When soil N supply exceeds plant N demand, N mineralized during the growing season is susceptible to loss (Paul and Zebarth, 1997b). Strategies to properly account for the soil N supply, to reduce N applications in excess of plant N requirements and to synchronize N supply and plant N uptake will be critical in reversing this trend.



3. Predictors of Soil N Supply in Humid Temperate Regions

Sharifi *et al.* (2007b) stated that a realistic estimate of N mineralized from SOM is essential for determining the rate of N fertilizer application required to optimize crop yield and quality, and to minimize adverse impacts of excess N on the environment. As mentioned above, soil N supply in humid regions is primarily dominated by in-season organic N mineralization due to substantial N losses over late fall and winter (Zebarth *et al.*, 2005) that vary within and between fields, as well as across years. Knowledge of the quantity of N that will potentially be available during the growing season is therefore important for improving N fertilizer management, and thus requires an estimation of the size of the labile organic N pool, which is degraded through microbial action to release plant-available N and provide the soil N supply (Curtin and Campbell, 2008).

While the size and quality of the potentially mineralizable N (N_0) (i.e., the maximum quantity of N that the soil can mineralize) is related to the soil N supply, laboratory methods assess plant-available N concentration under controlled conditions and therefore cannot predict how much will actually reach a crop due to transformations in the N cycle under specific soil and environmental conditions encountered in the field. A long-term aerobic incubation (AI) of >20 weeks under optimum temperature (35 °C) and moisture (-80 kPa) with period leaching of mineralized N was proposed by Stanford and Smith (1972) to estimate N_0 and its mineralization rate constant (k) using a first-order kinetic model. This method, used in its original form or modified, is generally regarded as the standard measure of N mineralization potential. However, it is time consuming and not practical for routine use. Several other laboratory methods, both biological and chemical, were developed as indices of N mineralization potential. The form of N measured by these different indices is given in Table 1.

The acceptance of an N index depends on its ability to routinely predict N_0 (Schomberg *et al.*, 2009; Sharifi *et al.*, 2007b; Wang *et al.*, 2001) as well as N supply in the field (Griffin, 2008). Examples of research using both of these approaches are summarized in Tables 2 and 3, respectively. Although most SON is proteinaceous in orgin (DiCosty *et al.*, 2003; Knicker, 2000, 2004), chemical methods that aim to extract these proteinaceous compounds from the soil and predict N supply across all agroecosystems are proving unsuccessful. These compounds are tightly bound to a nonextractable phase (Knicker, 2000; Knicker and Hatcher, 1997) and their cycling is controlled by the interaction of site-specific factors such as soil type, moisture, and temperature, microbial diversity, and agricultural management. Rovira *et al.* (2008) noted that there is no universal pattern of decomposition, suggesting the existence of site-specific biota. These factors may explain why certain soil testing methods give reliable estimates of soil N supply in one area, but not across broad geographical regions and agricultural practices.

3.1. Biological methods

The biological methods involve soil incubation under conditions that promote N mineralization and measure inorganic N produced during a specified period of time. They are based on the fact that N transformation in soils under field conditions involves microbial-based processes. Biological methods vary by soil pretreatment (wet vs. dry, sieved vs. intact), incubation procedures (varying temperature and moisture, aerobic vs. anaerobic), incubation periods (1–40 weeks), extracting solutions (1 M KCl, 2 M KCl, 0.01 M $CaCl_2$), and methods of determination (colorimetric vs. steam distillation). Both NH_4–N and NO_3–N are measured during AIs, but only NH_4–N is produced under anaerobic conditions. Unfortunately,

Table 1 Nitrogen forms measured by N indices

N index	Abbreviation	Form of N measured
Biological methods		
Aerobic incubation	AI	Soluble NH_4 and NO_3, N mineralized into NH_4 and NO_3
Anaerobic incubation	AnI	Soluble NH_4, N mineralized into NH_4
Chemical methods		
UV absorbance of $NaHCO_3$ extract at 205 nm	$NaHCO_3$–205	Soluble and exchangeable NH_4 and NO_3
UV absorbance of $NaHCO_3$ extract at 260 nm	$NaHCO_3$–260	Exchangeable NH_4 and hydrolyzable N
Hot KCl extractable N (100 °C)	H–KCl–N	Soluble and exchangeable NH_4, hydrolyzable N
Hot water extractable N (100 °C)	H–W–N	Soluble and exchangeable NH_4 and NO_3, clay-fixed NH_4
Direct steam distillation of NaOH extract	NaOH-DD	Exchangeable NH_4, amino sugars, amides, and some amino acids
Direct steam distillation of phosphate–borate buffer (pH 11.2) extract	PB-DD	Soluble and exchangeable NH_4, some amino acids
Gas pressure test with Ca $(ClO)_2$	GPT	Soluble and exchangeable NH_4, hydrolyzable N
Microbial biomass C and N	MBC, MBN	Total C and N in living microbial biomass
Illinois soil N test for amino sugar N	ISNT	Amino sugar N, some amino acids, and exchangeable NH_4
Particulate organic matter C and N	POMC, POMN	Total C and N of sand-size OM
Light fraction organic matter C and N	LFOMC, LFOMN	Total C and N of OM isolated by density fractionation
In situ methods		
Preplant nitrate test	PPNT	Soluble NO_3
Presidedress nitrate test	PSNT	Soluble NO_3
Anion and cation exchange membranes	AEM, CEM	Soluble NO_3 and NH_4

biological methods are unable to fully account for the frequent fluctuations in temperature and dry–wet cycles that occur under field conditions. The absence of plants in laboratory incubations is another limitation since plant

Table 2 Relationship between N indices and N_o determined by aerobic incubation

N index[a]	Duration of incubation (days)	Coefficient of determination (R^2)	Reference
H–KCl–N	168	0.13	Curtin and Wen (1999)
H–KCl–N	168	0.26	Sharifi *et al.* (2007b)
H–KCl–N	168	0.78	Jalil *et al.* (1996)
$NaHCO_3$-205	168	0.47	Sharifi *et al.* (2007b)
$NaHCO_3$-260	168	0.74	Sharifi *et al.* (2007b)
MBC	168	0.11	Sharifi *et al.* (2007b)
POMC	168	0.47	Sharifi *et al.* (2007b)
POMC	287	0.77	Schomberg *et al.* (2009)
POMN	168	0.39	Sharifi *et al.* (2007b)
ISNT	168	0.51	Sharifi *et al.* (2007b)
NaOH-DD	168	0.61	Sharifi *et al.* (2007b)
PB-DD	168	0.11	Sharifi *et al.* (2007b)
PB-DD	168	0.73	Jalil *et al.* (1996)
GPT	287	0.83[b] (0.57)[c]	Schomberg *et al.* (2009)

[a] Abbreviations as in Table 1.
[b] Correlation coefficient (*r*) from publication.
[c] Calculated coefficient of determination (R^2).

roots alter microbial diversity, soil moisture, and exude C that stimulates the N mineralization rate (Parkin *et al.*, 2002).

Although biological methods, particularly AIs, simulate N mineralization under field conditions, they have been regarded as time consuming, expensive, and not practical for routine use (Sharifi *et al.*, 2007b). Moreover, the absence of a standardized procedure makes it difficult to compare the correlation between this and other methods.

3.1.1. Aerobic incubation

A standard long-term incubation method was first proposed by Stanford and Smith (1972) involving soil incubation for >20 weeks under optimum temperature (35 °C) and moisture (−80 kPa) with periodical leaching of mineralized N with 0.01 M $CaCl_2$. The potentially mineralizable N (N_0) and its mineralization rate constant (k) were assessed using a first-order kinetic model. Several studies (Campbell *et al.*, 1984, 1988; Carpenter-Boggs *et al.*, 2000) showed that N_0 or k could be adjusted to provide a better estimate of N supply with respect to fluctuations in soil temperature and moisture that occur under field conditions. In a 40-week AI at 35 °C with organic-waste amended soils, Griffin and Laine (1983) reported that yield and N uptake of corn correlated well with the $N_0 \times k$ interaction, but N_0 alone proved to be a very poor predictor of yield or N uptake. Carpenter-Boggs *et al.* (2000)

Table 3 Relationship between N indices and N supply under field conditions

N index[a]	Field assessment	Coefficient of determination (R^2)	Reference
PPNT	Potato relative yield	0.58[b] (0.34)[c]	Sharifi *et al.* (2007a)
PPNT	N supply to corn[d]	0.75 (0.56)	Hong *et al.* (1990)
PPNT	N supply[e]	0.64	Sharifi *et al.* (2009c)
PSNT	N supply to corn	0.58	Fox *et al.* (1993)
H–KCl–N	Oats N uptake	0.79	Smith and Li (1993)
H–KCl–N	Potato relative yield[f]	0.09 (<0.01)	Sharifi *et al.* (2007a)
$NaHCO_3$-260	N supply to corn	0.86	Fox and Piekielek (1978b)
$NaHCO_3$-260	N supply to corn	0.41 (0.17)	Hong *et al.* (1990)
$NaHCO_3$-205	Potato relative yield	0.48 (0.23)	Sharifi *et al.*, 2007a
$NaHCO_3$-205	N supply	0.40	Sharifi *et al.* (2009c)
$NaHCO_3$-205	Corn yield[g]	0.83, 0.31	Nyiraneza *et al.* (2009)
MBN	Potato relative yield	0.19 (0.04)	Sharifi *et al.* (2007a)
POMC	Potato relative yield in one season[h]	0.12 (0.35)	Sharifi *et al.* (2007a)
POMN	Potato relative yield in one season	0.30 (0.55)	Sharifi *et al.* (2007a)
ISNT	EONR for Corn	0.87, 0.78	Williams *et al.* (2007b)
PB-DD	N supply to Corn	0.25 (0.1)	Hong *et al.* (1990)
AEM	Corn N uptake	0.52	Ziadi *et al.* (2006)
AEM	Canola N uptake	0.57[i], 0.86[j]	Qian and Schoenau (1995)
AEM	Corn N uptake[g]	0.91, 0.65	Nyiraneza *et al.* (2009)
NIRS	N supply to corn	0.49	Fox *et al.* (1993)

[a] Abbreviations as in Table 1.
[b] Correlation coefficient (*r*) from publication.
[c] Calculated coefficient of determination (R^2).
[d] Corn N uptake—0.75 (starter fertilizer N).
[e] Potato plant N uptake measured at vine desiccation plus soil mineral N at 0–30 cm at harvest.
[f] Mean of two growing seasons ($n = 40$).
[g] Two growing seasons (2005 and 2006, respectively).
[h] One growing season ($n = 19$).
[i] Thirty soils used.
[j] Twenty-three soils used.

incubated soils for 184 days in a variable-temperature incubator designed to mimic field soil temperatures, and reported a strong correlation ($r = 0.89$) between corn N uptake (no fertilizer N applied) and total N mineralized. The values of N_0 and k vary depending on temperature, moisture content, and incubation duration (Wang *et al.*, 2003). Therefore, to obtain an N_0

value that is unequivocally indicative of soil N mineralization capacity, Wang *et al*. (2003) suggested that the incubation should be conducted at standard temperature (35 °C) and moisture conditions (55–65% waterholding capacity or −30 to −10 kPa), and a standard mineralization rate constant ($k = 0.054$ week^{-1}) should be used for all soils. The standard k minimizes the effect of incubation duration from 20 to 40 weeks on N_0 (Wang *et al*., 2003). Short-term AI has been recommended as an alternative to long-term incubation, which eliminates the need for periodic leaching. In spite of inconsistent results, AI is more likely to simulate field conditions than other methods.

3.1.2. Anaerobic incubation

Short-term anaerobic incubation (ANI) is a rapid method to quantify the NH_4–N released under anoxic conditions in a soil–water slurry incubated for 7 or 14 days under anaerobic conditions (Curtin and Campbell, 2008; Schomberg *et al*., 2009). In contrast to AI, higher temperatures that lead to more rapid mineralization can be used, more N is usually mineralized, and there is no need to optimize moisture conditions. Nevertheless, differences in sample pretreatment that affect the N mineralized and the N mineralized by AI and ANI are not always related (Curtin and Campbell, 2008). Robinson (1967) correlated N mineralized from AI and ANI with soil organic C, Kjeldahl-N in the soil, leaf N concentration, and crop yield and concluded that AI values were more satisfactory than the ANI values in determining potentially available mineral N. Gianello and Bremner (1986a) reported correlation coefficients (r) of 0.85–0.96 between NH_4 released during a 7-day ANI and net N mineralized during AI at varying temperatures (30 and 35 °C) for 2 and 12 weeks, respectively.

3.2. Chemical extraction methods

Several chemical extraction methods (Table 1) were developed to estimate potentially available N and can be used as predictors of N supply. As noted by Griffin (2008), these methods are based on the hypothesis that a specific extractant releases N from a pool of similar decomposability but generally do not require that the N pool released by extraction is chemically homogeneous or biologically meaningful. They can be more rapid and precise than biological procedures (Curtin and Campbell, 2008), and produce an index of the contribution of soil N mineralization to soil N supply (Sharifi *et al*., 2007a). However, they do not account for the effects of environmental conditions or take into account losses of soil mineral N during the growing season due to leaching and denitrification (Sharifi *et al*., 2007a), and are not capable of simulating the microbial-mediated release of mineral N that occurs in incubated soil (Curtin and Campbell, 2008). The lack of

consistent and strong correlative relationships across climatic conditions, soils, and management scenarios has hindered widespread adoption of these methods. The AI procedure of Stanford and Smith (1972), in its original form or modified, is generally used as the reference for these methods.

3.2.1. Ultra violet absorbance of $NaHCO_3$-extractable N

The use of 0.01 M $NaHCO_3$ as a predictor of N supply was proposed by Maclean (1964). It is well known that organic N compounds accumulate in highly acidic soils, and that mineralization is accelerated by raising the soil pH. On this basis, it was assumed that a relationship exists between solubility and availability of N compounds to plants, and that extraction with a mild alkaline solution should simulate conditions produced by liming to near neutrality (Maclean, 1964). This method was modified by Fox and Piekielek (1978b) by using UV absorbance at 260 nm to measure extractable N in the extracts. Absorbance at 205 nm measures both organic and mineral N forms in the $NaHCO_3$ extract (Fox and Piekielek, 1978b; Sharifi *et al.*, 2007b), while absorbance at 260 nm measures OM content (Fox and Piekielek, 1978a). Sharifi *et al.* (2009c) showed that agricultural management effects, such as crop rotation are detected by absorbance at 205 nm but not at 260 nm. They explained that, in the short-term, crop rotation increases the proportion of labile organic N (referred to as "soil mineralizable N") in their study, but the SON content did not change. Several studies (Fox and Piekielek, 1978b; Hong *et al.*, 1990; Sharifi *et al.*, 2007a,b, 2009c) have reported strong correlations between soil NO_3–N concentration and absorbance at 205 nm than at 260 nm. Serna and Pomares (1992) reported that absorbance at 205 and 260 nm were correlated with N mineralization potential (16-week AI), however, correlations were stronger for absorbance at 260 nm ($R^2 = 0.70$) than at 205 nm ($R^2 = 0.60$) in light to medium soil texture. However, Serna and Pomares (1992) found that N uptake by corn grown in a growth chamber was better correlated to absorbance at 205 nm than at 260 nm ($R^2 = 0.74$ and 0.30, respectively). This illustrates a discrepancy between N mineralization potential and the N supply to crops, as detected by absorbance measurements. While it might suggest that plants access a different pool of SON than microorganisms, it could also reflect the fact that correlations do not distinguish between associative and cause-and-effect relationships. In the study by Serna and Pomares (1992), correlation coefficients between N mineralization potential and absorbance at 205 and 260 nm were higher in sandy than loamy or clay soils due to the tendency of clay soils to form microaggregates and to protect OM.

3.2.2. Hot KCl extractable N

Gianello and Bremner (1986b) proposed that the NH_4–N concentration of extracts from soil shaken with 2 M KCl at 100 °C for 4 h and corrected for the initial NH_4 concentration was an index of N_0. Hot KCl–N (H–KCl–N)

includes soluble and exchangeable forms of NH_4–N, the water-soluble fraction of organic N, and N compounds released from lysed of microbial cells (Sharifi *et al.*, 2007b, 2008b). Curtin and Wen (1999) found that H–KCl–N (corrected for initial NH_4) was not a good predictor of the cumulative amount of N mineralized after 24-week incubation at 35 °C ($R^2 = 0.25$) or of N_0 ($R^2 = 0.13$), but was a good predictor of N mineralized in the first 2 weeks of incubation ($R^2 = 0.69$). They suggested that hot KCl was selective for a water-soluble fraction of OM. However, when total NH_4 extracted in hot KCl was used (uncorrected for initial NH_4), the relationship with N_0 improved considerably ($R^2 = 0.55$). The reverse was reported by Sharifi *et al.* (2007b) in that H–KCl–N uncorrected for initial NH_4 was better related to N_0 than when corrected for initial NH_4 ($R^2 = 0.46$ and 0.26, respectively). Although the soils from both studies were chosen to represent various management regimes (different crops, crop rotations, tillage practices, and fertilizer treatments) and climatic zones (semi-arid to humid), soils from the Sharifi *et al.* (2007b) study had a smaller range and hence a lower mean organic C and N than those from the Curtin and Wen (1999) study. Another difference was that Sharifi *et al.* (2007b) found total organic C and total organic N highly correlated with N_0 ($R^2 = 0.60$ and 0.67, respectively), while Curtin and Wen (1999) found a low correlation between total N and N_0 ($R^2 = 0.13$). Soils used by Curtin and Wen (1999) also had higher clay contents, which can protect labile organic N fractions through surface adsorption and reduce the mineralization rate and mineralization potential. In addition, Curtin and Wen (1999) indicated that H–KCl–N was a good predictor of N_0 in soils where k (mineralization rate constant) does not vary greatly, so this test may not be appropriate for heavily manured soils. Hong *et al.* (1990) found that H–KCl–N was not a good predictor of N supply in Pennsylvania soils, many of which were well drained and heavily manured. The chemical nature of organic N hydrolyzed in hot KCl is still unknown.

3.2.3. Hot water extractable N

Hot water extractable N as an index of N_0 and predictor of N supply was proposed by Curtin *et al.* (2006). Nitrogen extracted by hot water consists of organic N (80%), and the remainder is NH_4–N generated by hydrolysis of heat-labile organic N. This method measures both organic N and NH_4–N, whereas only NH_4–N is measured in the hot KCl method. Ammonium N released by hot water at 80 °C was closely related to hot KCl. NH_4–N ($R^2 = 0.92$), though somewhat more NH_4–N was extracted in hot KCl (Curtin *et al.*, 2006). A study examining changes in hot water extracts of two contrasting soils (alkaline fluvisol and acid cambisol) during incubation found that humic materials produced by microbial growth and death were extracted in hot water (Redl *et al.*, 1990). These results suggest that the N released by hot water (80 °C) is mainly of microbial origin. However,

Chantigny *et al.* (2010) disputed the notion that hot water preferentially extracts N-rich microbial tissues and further suggested that NH_4–N released in hot water above 50 °C included clay-fixed NH_4.

3.2.4. Direct steam distillation with sodium hydroxide extract or phosphate–borate buffer extract (pH 11.2)

The NH_4–N liberated by direct distillation of soil with alkaline reagents such as sodium hydroxide (NaOH; Sharifi *et al.*, 2007b) or phosphate–borate buffer (PB; Gianello and Bremner, 1988; Hong *et al.*, 1990) were used as indices of mineralizable N. Direct distillation with NaOH was suggested by Sharifi *et al.* (2007b, 2009b), a modification of the procedure of Stanford (1978). According to Schomberg *et al.* (2009), NaOH-DD measures the most chemically resistant but hydrolyzable N pool and likely includes N from NH_4–N, amino sugars, amides, and certain amino acids (Sharifi *et al.*, 2007b, 2008b). A moderate relationship ($R^2 = 0.55$) was reported by Schomberg *et al.* (2009) between NaOH-DD and N mineralized after 41 weeks.

Curtin and Wen (1999) found the PB-DD was poorly related to N_0 ($R^2 = 0.09$), but was better related to N mineralized after the first 2 weeks of incubation ($R^2 = 0.64$). Good relationships between PB-DD and N_0 were reported by Jalil *et al.* (1996) ($R^2 = 0.73$) and Schomberg *et al.* (2009) ($R^2 = 0.54$). Curtin and Wen (1999) suggested that the PB solution extracts labile organic N adsorbed to mineral surfaces as well as more soluble organic N, while Gianello and Bremner (1986a, 1988) suggested that it measures a combination of NH_4–N and some amino acids. Sharifi *et al.* (2008a) reported that NaOH-DD extracted a greater portion of SON than PB-DD because NaOH-DD hydrolyzed organic N adsorbed to mineral surfaces and this alkaline solution (pH 14) extracted more soluble organic N than the PB (pH 11.2).

The NaOH-DD method is sensitive to management-induced changes such as tillage and crop rotation (Sharifi *et al.*, 2008a, 2009c). Sharifi *et al.* (2007b) compared NaOH-DD and PB-DD using contrasting soils from a wide range of climatic zones and management histories, and reported a better relationship for NaOH-DD than PB-DD with N mineralized after 24-week AI ($R^2 = 0.61$ and 0.11, respectively). Hong *et al.* (1990) examined the ability of PB-DD to predict the N supply to maize in Pennsylvania soils over 3 years and concluded that PB-DD was not a good predictor of soil N supply ($r = 0.25$). Conversely, Vanotti *et al.* (1995) showed that PB-DD was a good indicator of soil N supply under field conditions in Wisconsin ($r = 0.76$ and 0.80 for corn grain yield and N uptake, respectively) and cumulative N mineralized after 4 weeks ($r = 0.79$). Jalil *et al.* (1996) reported that PB-N-DD was effective in detecting the effect of crop rotation on soil N supply.

3.2.5. Gas pressure test

Gas pressure is generated when a strong oxidizing reagent such as $Ca(ClO)_2$ oxidizes NH_4 to N_2 gas and C to CO_2 in a closed vessel. This method was originally developed by Chescheir *et al.* (1985) to measure the NH_4 content of livestock manures and subsequently adopted by Picone *et al.* (2002) as a rapid (25 min) gas pressure test (GPT) to estimate mineralizable N and MBC in soils in Georgia. They reported strong correlation between the GPT and N mineralized in 24 days and soil MBC ($r = 0.77$ and 0.90, respectively). In mineral soils of North Carolina, Williams *et al.* (2007b) found significant relationships between the GPT and economically optimum N rate (EONR), and delta yield (maximum yield minus check yield) for corn ($R^2 = 0.62$ and 0.60, respectively). However, due to the low coefficients of determination obtained, Williams *et al.* (2007b) concluded that the GPT cannot be used to make N recommendations and should not be used in soils high in OM. Schomberg *et al.* (2009) reported that the GPT was not a good predictor of potentially mineralizable N of soils from southern USA ($R^2 = 0.57$). The GPT could be tested further in humid temperate soils, but mineral N transformations during the growing season may restrict its usefulness in predicting soil N supply.

3.2.6. Microbial biomass C and N

Soil microbial biomass is a relatively small component of the SOM—the MBC comprises only 1–3% of total soil C and MBN is 5% of total soil N—but they are the most biologically active and labile C and N pools (Deng *et al.*, 2000; Smith and Paul, 1990). The chloroform fumigation-direct extraction method of Vance *et al.* (1987), further described by Voroney *et al.* (2008), is the most common method to measure MBC and MBN concentrations.

Numerous studies have related MBC or MBN concentrations to N_0 in agroecosystems with contrasting results (Deng *et al.*, 2000; Franzluebbers *et al.*, 2001; Hu and Cao, 2007; Sharifi *et al.*, 2007b; Willson *et al.*, 2001). Carter and Macleod (1987) found that MBN was closely related to N_0 ($R^2 = 0.94$) in Prince Edward Island soils, while Sharifi *et al.* (2007b) reported that MBC was poorly related to N_0 ($R^2 = 0.11$) in soils from humid and semi-arid climatic zones in Canada and the USA. However, there are few reports in the literature that relate MBC or MBN (Sharifi *et al.*, 2007a) to soil N supply in arable crop fields in humid temperate regions. Microbial biomass in humid temperate regions is subjected to frequent variations in soil water potential, temperature, and substrate availability during the growing season. In deciduous forests, Holmes and Zak (1994) reported marked variability in net N mineralization during the growing season while MBC and MBN remained relatively constant. They concluded that N availability is not controlled by large seasonal fluctuations in soil microbial biomass, but rather by changes in the turnover rate of microbial biomass such that a relatively constant pool is maintained through time. Other studies also reported that the microbial biomass remains

relatively constant throughout the year in spite of changing soil conditions and nutrient availability (Patra *et al.*, 1990; Puri and Ashman, 1998). This may suggest that microbial activity, rather than the size of the microbial biomass represents a better indicator of soil N supply (Hassink *et al.*, 1993; Puri and Ashman, 1998). However, Deng *et al.* (2000) suggested that N mineralization is predominantly controlled by biochemical processes that are independent of microbial activity (i.e., from extracellular enzymes). Nevertheless, microbial activity and/or enzyme activity alone, or in combination with microbial biomass may not be ideal indicators of soil N supply since a substrate is required, and this can be influenced by amount/quality of crop residues, soil texture, moisture, and temperature.

3.2.7. Illinois soil N test for amino sugar N

Khan *et al.* (2001) and Mulvaney *et al.* (2001) noted that an estimate of a labile or organic N fraction that becomes available to the plant through mineralization during the growing season would be the ideal soil N test. This lead to the development of the Illinois soil N test (ISNT) on the assumption that the amino sugar N fraction was a good predictor of corn response to N fertilization. Khan *et al.* (2001) used the ISNT to positively identify soils that were unresponsive to fertilizer N. Mulvaney *et al.* (2001) reported that soil concentrations of amino sugar N were highly correlated with check-plot corn yield ($r = 0.79$) and fertilizer N response of corn in Illinois ($r = 0.82$). They further reported greater mineral N production in the nonresponsive soils with an accompanying reduction in amino sugar N. Also in Illinois, the ISNT was significantly related to corn N requirement and correctly identified 94% of the sites that were unresponsive to fertilizer N (Mulvaney *et al.*, 2006). The ISNT was strongly related to EONR for well and poorly drained sites in North Carolina ($R^2 = 0.87$ and 0.78, respectively) (Williams *et al.*, 2007a). In addition, Williams *et al.* (2007b) reported a strong relationship between ISNT and EONR ($R^2 = 0.90$) in mineral soils. Sharifi *et al.* (2007b) found a good correlation ($R^2 = 0.51$) between ISNT and potentially mineralizable N (AI at 25 °C for 24 weeks) in soils from humid and semi-arid regions across Canada and north-eastern USA. Conversely, Klapwyk and Ketterings (2006) and Barker *et al.* (2006b) found that the ISNT was unable to separate responsive and nonresponsive corn sites in New York and Iowa, respectively. However, Klapwyk and Ketterings (2006) reported improved prediction when OM was considered. There were no significant relationships between ISNT and relative grain yield, grain yield response, or EONR for corn (Barker *et al.*, 2006b) in Iowa. Other studies (Laboski *et al.*, 2008; Marriott and Wander, 2006; Sharifi *et al.*, 2007a) also found that the ISNT was poorly related to labile soil N and crop response to N fertilization. Yet, it was effective in accounting for potentially available N from previously applied compost and liquid dairy manure (Klapwyk *et al.*, 2006), crop rotation (Barker *et al.*, 2006a), and tillage practices at some sites (Sharifi *et al.*, 2008a).

These inconsistent results, particularly from field evaluations, can be attributed to differences in agricultural practices (manure, crop rotation and tillage system; Barker *et al.*, 2006a; Laboski *et al.*, 2008; Sharifi *et al.*, 2007a, 2008a), climate variability (Barker *et al.*, 2006b; Laboski *et al.*, 2008), and differences in soil characteristics including total soil C and N. For example, at L'Acadie in Quebec, Canada, SON concentration and ISNT values varied significantly ($P < 0.05$) according to tillage system (Sharifi *et al.*, 2008a). It is important to note that the unresponsive sites identified by the ISNT in the study by Khan *et al.* (2001) historically received manure; therefore, it can be argued that the ISNT was responding to manure application history. In the study by Laboski *et al.* (2008), the previous crop and drainage class significantly ($P < 0.05$) affected the ISNT values. The soils used by Barker *et al.* (2006b) had relatively high levels of hydrolyzable NH_4–N relative to amino sugar N. Mean soil OM content in soils used by Klapwyk and Ketterings (2006) was twice that of soils used by Khan *et al.* (2001).

The ISNT may not be selective for amino sugar N, but most likely extracts multiple fractions of soil N (Griffin, 2008; Olk, 2008a). Nevertheless, Wang *et al.* (2003) concluded that the determination of any one chemical form or combination of forms of organic N may not be sufficient in estimating N_0 if other soil properties vary widely. This is evident in the different results reported in the literature. For example, the range of OM levels in the study by Klapwyk and Ketterings (2006) was much larger than in the study by Khan *et al.* (2001). However, the OM range was similar for studies by Khan *et al.* (2001) and Sharifi *et al.* (2007a), but with differing crops (corn vs. potato). There are currently no reports of successful field evaluations of the ISNT with crops other than corn.

3.2.8. Light fraction organic matter carbon and nitrogen (LFOMC, LFOMN), and particulate organic matter carbon and nitrogen

Light fraction organic matter (LFOM) and particulate organic matter (POM) are mainly composed of partially decomposed plant residues together with microbial products that are not closely associated with soil minerals (Six *et al.*, 2002). They are also referred to as physically uncomplexed OM or the intermediate pool of OM between fresh plant residues and stabilized soil organic matter (Gregorich *et al.*, 2006a), are the major sources of C and N for microbes and represent the major pathway through which N is transformed from crop residues to the soil (Haynes, 2005). Several studies have demonstrated the response of these parameters to soil management and cropping systems, but because of their nature, they reflect short-term dynamics in the SOM pool (Angers *et al.*, 1993; Franzluebbers and Stuedemann, 2008; Franzluebbers *et al.*, 2000; Griffin and Porter, 2004; Janzen *et al.*, 1992; Willson *et al.*, 2001). These fractions have a higher turnover rate than total SOM (Chan, 1997, 2001). While they may exist in the same labile N pool, they differ in characteristics and association.

POM, also referred to as macroorganic matter, or sand-size or coarse POM, is associated only with the sand-sized fraction and are separated through sieving. The LFOM, also referred to as noncombined clay fraction and mineral-free debris, may be present in all particle-size fractions and are isolated by using liquids of a specific density (1.2–2 g cm^{-3}) such as NaI (Gregorich *et al.*, 2006a; Gregorich and Beare, 2008). According to Gregorich *et al.* (2006a), the amount of soil C and N in POM is often greater than that in LF. In addition, LFOM is more closely related to plant residues than POM, and POM has a lower C/N ratio than LFOM. In agricultural soils, POM accounts for about 22% and 18% of soil organic C and total soil N respectively, while LFOM makes up 8% and 5%, respectively. The C/N ratio of these fractions is usually wider than that of the whole soil and therefore may immobilize mineralized N (Janzen *et al.*, 1992). A study by Compton and Boone (2002) showed that LF immobilized more ^{15}N per unit of C than POM due to a greater C/N ratio. Whalen *et al.* (2000) observed that the addition of LF to soils caused N immobilization and concluded that POM was the main source of potentially mineralizable N, whereas LF is a potential sink for mineral N.

In using soils from the different agroecological regions of Saskatchewan, Curtin and Wen (1999) found a good correlation between LFOM and potentially mineralizable N ($R^2 = 0.83$), however, it was not well related to N mineralized in the first 2 weeks of incubation. There are very few reports in the literature that relate either of these fractions to soil N supply under field conditions. Particulate organic matter C (POMC) was poorly related to total N uptake and potato relative yield across sites in USA and Canada ($r = 0.32$ and 0.35, respectively), however, particulate organic matter nitrogen (POMN) had a higher correlation ($r = 0.41$ and 0.55, respectively) (Sharifi *et al.*, 2007a). In a subsequent study, Sharifi *et al.* (2008b) reported good predictive potential of POMN with total N uptake and N uptake + soil mineral N ($R^2 = 0.51$ and 0.66, respectively) after harvest in a potato production system in Maine. Due to their association with microbial biomass (Franzluebbers and Stuedemann, 2003; Janzen *et al.*, 1992), accumulation of these fractions can occur during fall and winter. Their subsequent mineralization in the spring and summer depends on moisture and temperature, but may not show a consistent pattern. Hence, a better understanding of the nutrient supply capabilities of these fractions is required.

3.3. *In situ* methods

Several *in situ* methods such as buried resin bags and microplot cylinders could be used to assess plant-available N, but this chapter will focus on ion exchange membranes buried randomly in the field with no barriers to capture NO_3–N and NH_4–N from the soil solution. In addition, the preplant nitrate test (PPNT) and presidedress nitrate test (PSNT) are

regarded as *in situ* methods due to the time the soil is sampled and form of N measured (NO_3–N) by these methods. These *in situ* methods cannot be used to predict N supply since they represent plant-available N accumulated during a short period during the growing season.

3.3.1. Preplant nitrate test

The PPNT or spring soil nitrate test measures soil NO_3 concentration within the crop root zone. Soil NO_3–N concentration at this stage represents residual soil NO_3 from the previous growing season and limited N mineralization that occurs in early spring (Zebarth *et al.*, 2009). Use of the PPNT alone is not reliable in humid regions since soil N supply is controlled by N mineralization during the growing season (Zebarth *et al.*, 2005). Bélanger *et al.* (2001) reported that the PPNT alone could not adequately predict the N requirement of potatoes in Atlantic Canada, while O'Halloran *et al.* (2004) found that the PPNT was unable to delineate management zones for barley and corn in southwestern Ontario. Conversely, Sharifi *et al.* (2008b) reported a good relationship ($R^2 = 0.58$) between PPNT and potato N uptake and concluded that the PPNT has the capacity to estimate soil N supply in the field, while Bilbao *et al.* (2004) reported that the PPNT gave an accurate estimate of optimum N rate for sugar beet in Mediterranean soils with limited leaching. The PPNT was a good predictor of soil N supply in a nonamended potato field (Sharifi *et al.*, 2007a). However, Sharifi *et al.* (2007a) noted that the PPNT was problematic as a predictive test in humid regions because soil NO_3–N concentrations can change rapidly during spring, making the values sensitive to sampling date, and therefore, may be more applicable in arid and subhumid environments. McTaggart and Smith (1993) attempted to estimate N_0 using the PPNT and concluded that PPNT was not a practical method for determining spring fertilizer applications in eastern Scotland. These findings suggest that the PPNT is unable to fully and consistently account for N mineralization during the growing season, and may be incapable of detecting management-induced changes on potentially mineralizable N in humid temperate regions.

3.3.2. Presidedress nitrate test

The PSNT was developed to improve N fertilization for corn in humid regions (Magdoff *et al.*, 1984), and is based on the assumption that the amount of NO_3–N present just before rapid plant N uptake is directly related to the soil N supply during the growing season. Soil NO_3–N concentration represents the residual NO_3–N from the previous growing season, N mineralized from manure application and/or fertilizer N application in early spring, and N mineralized from SOM up to sampling time (generally June–July). Nitrogen mineralized from SOM prior to sampling may be as much as 60% of apparent growing season soil N mineralization (Zebarth *et al.*, 2001). Schepers and Meisinger (1994) stated that the late spring increase in NO_3–N from *in situ*

mineralization depends on recent additions of crop residues or manure. The PSNT was developed for corn as a sidedress fertilizer management tool, and requires careful sampling within a short period of time and rapid analysis. Soil NO_3–N concentration between 21 and 25 mg kg^{-1} indicates sufficient N for corn to attain optimum yield (Fox *et al.*, 1989), and lower values suggest that sidedress N fertilizer application is required. However, frequent rainfall, large spatial variability and rapid changes in soil NO_3–N concentrations in humid regions (Ma *et al.*, 2007), coupled with sampling time, labor requirement, and cost have made it difficult to rely on the PSNT. Hence, it is better suited for identifying sites for which a yield response to additional N at sidedress is unlikely to occur, than for predicting the amount of fertilizer N required during the entire growing season (Klausner *et al.*, 1993). Heckman *et al.* (2002) indicated that the PSNT is most useful in cropping situations where significant amounts of mineral N may be expected in the soil prior to the period of major N uptake by the crop, especially in situations where manure was applied, or where forage crops were included in the rotation. The PSNT has been used in other crops such as sweet corn (Heckman *et al.*, 1995; Ma *et al.*, 2007), fall-grown cabbage (*Brassica oleracae* L.; Heckman *et al.*, 2002), lettuce (*Lactuca sativa* L.), and celery (*Apium graveolens* L.; Hartz *et al.*, 2000). Essentially, determination of critical soil NO_3–N concentration at the critical crop growth stage is vital for the success of the PSNT.

3.3.3. Anion and cation exchange membranes

In situ ion exchange membranes measure soil N supply at certain points in time since they are exposed to the same environmental conditions and edaphic factors that affect N mineralization and subsequent N uptake by plant roots (Qian *et al.*, 1992; Qian and Schoenau, 2002; Subler *et al.*, 1995; Ziadi *et al.*, 2006). However, this method cannot be used to predict N supply and is labor-intensive, especially due to the large number of samples required to identify treatment differences due to spatial variability in N mineralization.

According to Sharifi *et al.* (2009a), ion exchange membranes act as sinks similar to plant roots, and provide an index of actual N supply over time in soils. This index can be affected by duration of the membrane burial in the soil, competing sinks (microbes and roots), waterlogging, and landscape variations (Qian and Schoenau, 2002; Ziadi *et al.*, 1999). Ziadi *et al.* (2000) found a significant relationship between NO_3–N sorbed on anion exchangs membrane (AEM) and EONR ($R^2 = 0.45$) as well as relative forage yield in Quebec ($R^2 = 0.60$). A strong relationship between cumulative N uptake by forages and NO_3–N sorbed on AEM over two seasons ($R^2 = 0.92$ and 0.88 in spring 1995 and 1996, respectively) from four sites in Quebec was reported by Ziadi *et al.* (1999). Ziadi *et al.* (1999) also reported that NO_3–N sorbed on AEMs were significantly correlated to NO_3–N extracted by water, and that forage N uptake was better related to NO_3–N sorbed on AEMs than to NO_3–N extracted by water. Sharifi *et al.* (2009a)

used Plant Root Simulator probes (PRS^{TM}) that contained ion exchange membranes encapsulated in plastic probes to measure soil N supply in potato fields in Prince Edward Island and Nova Scotia. They found strong linear relationships between cumulative N supply rate at 31 days after planting measured by PRS^{TM} and total N uptake measured at vine removal ($R^2 = 0.60$), and total N uptake plus soil mineral N in 0–30 cm at harvest ($R^2 = 0.60$). Ziadi *et al.* (2006) reported significant relationships between NO_3–N adsorbed on AEMs and extracted by water in forage production ($R^2 = 0.95$), extracted by 2 M KCl in corn production ($R^2 = 0.66$), cumulative N uptake by forages ($R^2 = 0.94$), and N uptake by grain corn ($R^2 = 0.52$). Nyiraneza *et al.* (2009) also found good relationships between NO_3–N adsorbed on AEM (2 M KCl extraction) measured over two growing seasons (2005 and 2006) and corn yield ($R^2 = 0.83$ and 0.63, respectively) and N uptake ($R^2 = 0.91$ and 0.65, respectively). Using soils from Saskatchewan in two growth chamber experiments (30 soils in experiment 1 and 24 soils in experiment 2) and ANI, Qian and Schoenau (2005) reported significant relationships between NH_4–N sorbed on cation exchange membranes (CEMs) and N uptake by canola ($R^2 = 0.67$ and 0.73 in experiments 1 and 2, respectively).

Zebarth *et al.* (2009) stated that ion exchange membranes are most valuable when a rapidly growing crop depletes the soil mineral N sufficiently that direct measurement of soil mineral N during the growing season does not provide a meaningful estimate of plant-available N. Ion exchange membranes are superior to traditional *in situ* methods since they allow for minimal soil disturbance, ensure complete contact with the soil, measure mineral N fluxes that occur with changing environmental conditions over time, and reflect the cumulative effects of soil chemical, physical, and biological properties, as well as agricultural practices such as tillage, crop rotation, and manure application. However, like most other methods, there are limitations. Although a large number of membranes can be placed in the field, the actual size of the membranes and hence sampling area is relatively small. Also, the flux cannot be converted to relevant values for developing fertilizer recommendations. Moreover, the soil N supply varies from year to year, so the flux measurements from ion exchange membranes are not predictive.

3.4. Optical method

3.4.1. Near-infrared reflectance spectroscopy

The methods described previously are based on wet chemistry, sometimes require hazardous chemicals, and are expensive and time consuming. Near-infrared reflectance spectroscopy (NIRS) is an alternative method that is rapid, cost-effective, nondestructive, and environmentally safe (Dunn *et al.*, 2002; Galvez-Sola *et al.*, 2009; Nduwamungu *et al.*, 2009b). Near-infrared reflectance mainly measures overtones and combination bands of vibrations

of O–H, N–H, and C–H bonds found in organic constituents and in soil mineral particles (Sorensen and Dalsgaard, 2005). Therefore, direct quantitative estimates of NIR-spectra are impossible. Data are interpreted with multivariate statistics such as partial least squares regression, multiple linear regression, and principal components analysis (Börjesson *et al.*, 1999; Chang *et al.*, 2001). Coefficient of determination (R^2), ratio of performance deviation (RPD), ratio of error range (RER), and regression coefficient (b) were used by Nduwamungu *et al.* (2009b) to compare NIRS predictions with soil attributes in Eastern Canada. Calibration libraries will need to be validated against reference data on the same samples, before predicting concentrations of constituents in unknown samples (Malley *et al.*, 2002). The standard error in reference data (SER) should be reported, along with the standard error of prediction (SEP; Nduwamungu *et al.*, 2009a).

Nduwamungu *et al.* (2009a) discussed the application of NIRS for assessing primary and secondary soil properties. Primary properties that have a theoretical basis for NIRS predictions include particle size, moisture content, organic C, and total N, while secondary properties such as EC, CEC, pH, potentially mineralizable N, and microbial biomass have no theoretical basis but are correlated to certain primary properties. Moreover, portable NIRS have potential for "on site" determination of soil properties such as OM ($R^2 > 0.85$), CEC ($R^2 > 0.85$), and moisture content ($R^2 > 0.94$) (Sudduth and Hummel, 1993a,b). Vasques *et al.* (2009) used NIRS to predict total SOC and SOC fractions in soils in Florida and reported coefficients of determination (R^2) ranging from 0.42 to 0.70. Reeves and Van Kessel (2000) reported that NIRS successfully determined moisture ($R^2 = 0.95$), total C ($R^2 = 0.95$), total N ($R^2 = 0.96$), and NH_3–N ($R^2 = 0.97$) concentrations in dairy manures. Nduwamungu *et al.* (2009b) accurately predicted soil texture, CEC, total C, total N, and potentially mineralizable N in noncalcareous soils in Quebec, Canada, and NIRS successfully predicted soil nutrient concentrations and properties in other soils (Chang *et al.*, 2001; Cozzolino and Morón, 2003; Malley *et al.*, 1999; Martin *et al.*, 2002). The NIRS was used to predict N supply in corn ($R^2 = 0.49$; Fox *et al.*, 1993) and winter wheat ($R^2 = 0.81$; Börjesson *et al.*, 1999).

The use of NIRS for predicting soil N supply is promising, particularly with homogeneous soil samples, but requires further development of standard reference methods (biological or chemical) and a large spectral library.

4. Conclusions and Future Work

Numerous methods that measure N mineralization potential have been tested for their ability to predict soil N supply, but none has proven robust enough for broad acceptance. An ideal method would predict the

crop N uptake during the growing season, be inexpensive and rapid, and respond to N dynamics as influenced soil properties, agricultural practices, and environmental conditions. Soil N supply therefore appears to be system-specific, that is, it differs according to crop rotation, tillage system, organic amendment, soil properties, and most importantly, environmental conditions. This is evident since in many instances, an N test that has proven successful in one system failed to accurately predict the soil N supply in another. Therefore, accurate determination of N availability during a growing season in humid environments requires a holistic approach that considers a specific system. The following represents possible alternatives to current methodologies.

4.1. Combination of N indices plus modeling with weather data

A single N index is insufficient to predict the contribution of N mineralization to soil N supply for agroecosystems at a regional scale. Hence, a combination of N indices that are best suited for the particular system in conjunction with weather forecasts may be more accurate. Schomberg *et al.* (2009) showed that combining indices that represent an available substrate (e.g., total N) and microbial biomass (e.g., flush of CO_2 during 3 days; Franzluebbers *et al.*, 2000) can improve predictions of N_0 but the choice of indices depends on clay mineralogy and OM content. Kay *et al.* (2006) showed that variation in N supply can be explained by the interaction between the temporal variation in weather and the spatial variation in soil characteristics. Moreover, Kay *et al.* (2006) reported that early season rainfall exerted a greater influence on N supply than rainfall later in the season, so N fertilizer recommendations could be adjusted based on early season weather conditions. Dessureault-Rompre *et al.* (2010) integrated soil and climatic parameters to explain 63% of the variation in N_0 across Canada by combining a soil texture, a SOM, and a climatic parameter. However, the influence of agricultural practices such as tillage, crop rotation, and organic amendment application which are known to influence the soil mineralizable N pool were not considered. Therefore, more research is needed to evaluate the potential of combined soil N supply predictors in association with early season weather data across different agricultural practices.

4.2. Identification and quantification a specific N fraction that contributes to N supply

A good soil N test for temperate humid regions would measure plant-available N plus the organic N pool that makes a dominant contribution to N supply. Identifying the labile N forms in soils that supply the plant-available N pool and quantifying their turnover rate, as a function of soil

moisture and temperature, soil properties, and agricultural practices, will enhance the development and adoption of the appropriate test. For example, the development and use of the ISNT for amino sugar N by Khan *et al.* (2001) and Mulvaney *et al.* (2001) was based on this concept and identified sites that were unresponsive to N fertilization. Although the ISNT may not be selective for amino sugar N (Griffin, 2008; Olk, 2008a), it is important to note that the unresponsive sites identified by the ISNT historically received manure (Khan *et al.*, 2001); therefore, it can be argued that the ISNT was responding to manure application history. Subsequent evaluations of the ISNT across nonmanured, crop rotation or tillage sites were not very promising. This suggests that the dominant pool varies according to the production system as well as the soil properties and climatic condition.

REFERENCES

Abadín, J., González-Prieto, S. J., and Carballas, T. (2010). Relationships among main soil properties and three N availability indices. *Plant Soil* **339,** 193–208.

Acosta, V., and Tabatabai, M. A. (2001). Tillage and residue management effects on arylamidase activity in soils. *Biol. Fertil. Soils* **34,** 21–24.

Adamczyk, B., Smolander, A., Kitunen, V., and Godlewski, M. (2010). Proteins as nitrogen source for plants: A short story about exudation of proteases by plant roots. *Plant Signal. Behav.* **5,** 817–819.

Agehara, S., and Warncke, D. D. (2005). Soil moisture and temperature effects on nitrogen release from organic nitrogen sources. *Soil Sci. Soc. Am. J.* **69,** 1844–1855.

Almaraz, J. J., Mabood, F., Zhou, X., Madramootoo, C., Rochette, P., Ma, B. L., and Smith, D. L. (2009). Carbon dioxide and nitrous oxide fluxes in corn grown under two tillage systems in southwestern Quebec. *Soil Sci. Soc. Am. J.* **73,** 113–119.

Angers, D. A., N'Dayegamiye, A., and Cote, D. (1993). Tillage-induced differences in organic matter of particle-size fractions and microbial biomass. *Soil Sci. Soc. Am. J.* **57,** 512–516.

Baggs, E. M., Stevenson, M., Pihlatie, M., Regar, A., Cook, H., and Cadisch, G. (2003). Nitrous oxide emissions following application of residues and fertiliser under zero and conventional tillage. *Plant Soil* **254,** 361–370.

Barker, D. W., Sawyer, J. E., and Al-Kaisi, M. M. (2006a). Assessment of the amino sugar-nitrogen test on Iowa Soils: I. Evaluation of soil sampling and corn management practices. *Agron. J.* **98,** 1345–1351.

Barker, D. W., Sawyer, J. E., Al-Kaisi, M. M., and Lundvall, J. P. (2006b). Assessment of the amino sugar-nitrogen test on Iowa Soils: II. Field correlation and calibration. *Agron. J.* **98,** 1352–1358.

Beauchamp, E. G. (1997). Nitrous oxide emission from agricultural soils. *Can. J. Soil Sci.* **77,** 113–123.

Bélanger, G., Walsh, J. R., Richards, J. E., Milburn, P. H., and Ziadi, N. (2000). Comparison of three statistical models describing potato yield response to nitrogen fertilizer. *Agron. J.* **92,** 902–908.

Bélanger, G., Walsh, J. R., Richards, J. E., Milburn, P. H., and Ziadi, N. (2001). Predicting nitrogen fertilizer requirements of potatoes in Atlantic Canada with soil nitrate determination. *Can. J. Soil Sci.* **81,** 535–544.

Bélanger, G., Ziadi, N., Walsh, J. R., Richards, J. E., and Milburn, P. H. (2003). Residual soil nitrate after potato harvest. *J. Environ. Qual.* **32,** 607–612.
Bilbao, M., Martinez, J. J., and Delgado, A. (2004). Evaluation of soil nitrate as a predictor of nitrogen requirement for sugar beet grown in a mediterranean climate. *Agron. J.* **96,** 18–25.
Börjesson, T., Stenberg, B., Lindén, B., and Jonsson, A. (1999). NIR spectroscopy, mineral nitrogen analysis and soil incubations for the prediction of crop uptake of nitrogen during the growing season. *Plant Soil* **214,** 75–83.
Breland, T. (1994). Measured and predicted mineralization of clover green manure at low temperatures at different depths in two soils. *Plant Soil* **166,** 13–20.
Brookes, P. C., Kemmitt, S. J., Addiscott, T. M., and Bird, N. (2009). Reply to Kuzyakov *et al.*'s comments on our paper: 'Kemmitt, S. Lanyon, C. V., Waite, I. S., Wen, Q., O'Donnell, A. G., Brookes, P. C., 2008. Mineralization of native soil organic matter is not regulated by the size, activity or composition of the soil microbial biomass—A new perspective. *Soil Biol. Biochemi.* **40,** 61–73, **41,** 440–443.
Burton, D. L., and Beauchamp, E. C. (1984). Field techniques using the acetylene blockage of nitrous oxide reduction to measure denitrification. *Can. J. Soil Sci.* **64,** 555–562.
Burton, D. L., Zebarth, B. J., Gillam, K. M., and MacLeod, J. A. (2008). Effect of split application of fertilizer nitrogen on N_2O emissions from potato. *Can. J. Soil Sci.* **88,** 229–239.
Campbell, C. A., Myers, R. J. K., and Weier, K. L. (1981). Potentially mineralizable nitrogen, decomposition rates and their relationship to temperature for five Queensland soils. *Aust. J. Soil Res.* **19,** 323–332.
Campbell, C. A., Jame, Y. W., and Winkleman, G. E. (1984). Mineralization rate constants and their use for estimating nitrogen mineralization in some Canadian prairie soils. *Can. J. Soil Sci.* **64,** 333–343.
Campbell, C. A., Jame, Y. W., and de Jong, R. (1988). Predicting net nitrogen mineralization over a growing season: Model verification. *Can. J. Soil Sci.* **68,** 537–552.
Carpenter-Boggs, L., Pikul, J. L. Jr., Vigil, M. F., and Riedell, W. E. (2000). Soil nitrogen mineralization influenced by crop rotation and nitrogen fertilization. *Soil Sci. Soc. Am. J.* **64,** 2038–2045.
Carter, M. R., and Macleod, J. A. (1987). Biological properties of some Prince Edward Island soils: Relationship between microbial biomass nitrogen and mineralizable nitrogen. *Can. J. Soil Sci.* **67,** 333–340.
Centre de référence en agriculture et agroalimentaire du Québec. (2003). Fertilisation Reference Guide 1st edn. CRAAQ, Québec, QC, Canada (in French).
Chan, K. Y. (1997). Consequences of changes in particulate organic carbon in vertisols under pasture and cropping. *Soil Sci. Soc. Am. J.* **61,** 1376–1382.
Chan, K. Y. (2001). Soil particulate organic carbon under different land use and management. *Soil Use Manage.* **17,** 217–221.
Chang, C., Janzen, H. H., and Cho, C. M. (1998). Nitrous oxide emission from long-term manured soils. *Soil Sci. Soc. Am. J.* **62,** 677–682.
Chang, C.-W., Laird, D. A., Mausbach, M. J., and Hurburgh, C. R. Jr. (2001). Near-infrared reflectance spectroscopy-principal components regression analyses of soil properties. *Soil Sci. Soc. Am. J.* **65,** 480–490.
Chantigny, M. H., Prévost, D., Angers, D. A., Vézina, L.-P., and Chalifour, F.-P. (1996). Microbial biomass and N transformations in two soils cropped with annual and perennial species. *Biol. Fertil. Soils* **21,** 239–244.
Chantigny, M. H., Prevost, D., Angers, D. A., Simard, R. R., and Chalifour, F.-P. (1998). Nitrous oxide production in soils cropped to corn with varying N fertilization. *Can. J. Soil Sci.* **78,** 589–596.
Chantigny, M. H., Angers, D. A., Morvan, T., and Pomar, C. (2004). Dynamics of pig slurry nitrogen in soil and plant as determined with ^{15}N. *Soil Sci. Soc. Am. J.* **68,** 637–643.

Chantigny, M. H., Curtin, D., Beare, M. H., and Greenfield, L. G. (2010). Influence of temperature on water-extractable organic matter and ammonium production in mineral soils. *Soil Sci. Soc. Am. J.* **74,** 517–524.

Chatskikh, D., and Olesen, J. E. (2007). Soil tillage enhanced CO_2 and N_2O emissions from loamy sand soil under spring barley. *Soil Tillage Res.* **97,** 5–18.

Chescheir, G. M. I., Westerman, P. W., and Safley, L. M. (1985). Rapid methods for determining nutrients in livestock manures. *Trans. Am. Soc. Agric. Eng.* **28,** 1817–1824.

Chirinda, N., Carter, M. S., Albert, K. R., Ambus, P., Olesen, J. E., Porter, J. R., and Petersen, S. O. (2010). Emissions of nitrous oxide from arable organic and conventional cropping systems on two soil types. *Agric. Ecosyst. Environ.* **136,** 199–208.

Compton, J. E., and Boone, R. D. (2002). Soil nitrogen transformations and the role of light fraction organic matter in forests soils. *Soil Biol. Biochem.* **34,** 933–943.

Constantin, J., Mary, B., Laurent, F., Aubrion, G., Fontaine, A., Kerveillant, P., and Beaudoin, N. (2010). Effects of catch crops, no till and reduced nitrogen fertilization on nitrogen leaching and balance in three long-term experiments. *Agric. Ecosyst. Environ.* **135,** 268–278.

Cozzolino, D., and Morón, A. (2003). The potential of near-infrared reflectance spectroscopy to analyse soil chemical and physical characteristics. *J. Agric. Sci.* **140,** 65–71.

Curtin, D., and Campbell, C. A. (2008). Mineralizable nitrogen. *In* "Soil Sampling and Methods of Analysis" (M. R. Carter and E. G. Gregorich, Eds.), pp. 599–606. CRC Press, Boca Raton, FL.

Curtin, D., and Wen, G. (1999). Organic matter fractions contributing to soil nitrogen mineralization potential. *Soil Sci. Soc. Am. J.* **63,** 410–415.

Curtin, D., Wright, C. E., Beare, M. H., and McCallum, F. M. (2006). Hot water-extractable nitrogen as an indicator of soil nitrogen availability. *Soil Sci. Soc. Am. J.* **70,** 1512–1521.

Dambreville, C., Morvan, T., and Germon, J.-C. (2008). N_2O emission in maize-crops fertilized with pig slurry, matured pig manure or ammonium nitrate in Brittany. *Agric. Ecosyst. Environ.* **123,** 201–210.

Dancer, W. S., Peterson, L. A., and Chesters, G. (1973). Ammonification and nitrification of N as influenced by soil pH and previous N treatments. *Soil Sci. Soc. Am. J.* **37,** 67–69.

Davis, J. H., Griffith, S. M., Horwath, W. R., Steiner, J. J., and Myrold, D. D. (2008). Denitrification and nitrate consumption in an herbaceous riparian area and perennial ryegrass seed cropping system. *Soil Sci. Soc. Am. J.* **72,** 1299–1310.

De Jong, R., Yang, J. Y., Drury, C. F., Huffman, E. C., Kirkwood, V., and Yang, X. M. (2007). The indicator of risk of water contamination by nitrate-nitrogen. *Can. J. Soil Sci.* **87,** 179–188.

De Neve, S., and Hofman, G. (2002). Quantifying soil water effects on nitrogen mineralization from soil organic matter and from fresh crop residues. *Biol. Fertil. Soils* **35,** 379–386.

De Neve, S., Hartmann, R., and Hofman, G. (2003). Temperature effects on N mineralization: Changes in soil solution composition and determination of temperature coefficients by TDR. *Eur. J. Soil Sci.* **54,** 49–62.

Delin, S., and Lindén, B. (2002). Relations between net nitrogen mineralization and soil characteristics within an arable field. *Acta Agric. Scand. B* **52,** 78–85.

Deng, S. P., and Tabatabai, M. A. (1996). Effect of tillage and residue management on enzyme activities in soils. I. Amidohydrolases. *Biol. Fertil. Soils* **22,** 202–207.

Deng, S. P., and Tabatabai, M. A. (2000). Effect of cropping systems on nitrogen mineralization in soils. *Biol. Fertil. Soils* **31,** 211–218.

Deng, S. P., Moore, J. M., and Tabatabai, M. A. (2000). Characterization of active nitrogen pools in soils under different cropping systems. *Biol. Fertil. Soils* **32,** 302–309.

Dessureault-Rompre, J., Zebarth, B. J., Burton, D. L., Sharifi, M., Cooper, J. M., and Grant, C. A. (2010). Relationships among mineralizable soil nitrogen, soil properties, and climatic indices. *Soil Sci. Soc. Am. J.* **74,** 1218–1227.

Dharmakeerthi, R. S., Kay, B. D., and Beauchamp, E. G. (2005). Factors contributing to changes in plant available nitrogen across a variable landscape. *Soil Sci. Soc. Am. J.* **69,** 453–462.

DiCosty, R. J., Weliky, D. P., Anderson, S. J., and Paul, E. A. (2003). ^{15}N-CPMAS nuclear magnetic resonance spectroscopy and biological stability of soil organic nitrogen in whole soil and particle-size fractions. *Org. Geochem.* **34,** 1635–1650.

Drury, C. F., Findlay, W. I., and McKenney, D. J. (1992). Nitric oxide and nitrous oxide production from soil: Water and oxygen effects. *Soil Sci. Soc. Am. J.* **56,** 766–770.

Drury, C. F., Findlay, W. I., Gaynor, J. D., and McKenney, D. J. (1993). Influence of tillage on nitrate loss in surface runoff and tile drainage. *Soil Sci. Soc. Am. J.* **57,** 797–802.

Drury, C. F., Tan, C. S., Gaynor, J. D., Oloya, T. O., and Welacky, T. W. (1996). Water quality: Influence of controlled drainage-subirrigation on surface and tile drainage nitrate loss. *J. Environ. Qual.* **25,** 317–324.

Drury, C. F., Zhang, T. Q., and Kay, B. D. (2003). The non-limiting and least limiting water ranges for soil nitrogen mineralization. *Soil Sci. Soc. Am. J.* **67,** 1388–1404.

Drury, C. F., Reynolds, W. D., Tan, C. S., Welacky, T. W., Calder, W., and McLaughlin, N. B. (2006). Emissions of nitrous oxide and carbon dioxide: Influence of tillage type and nitrogen placement depth. *Soil Sci. Soc. Am. J.* **70,** 570–581.

Dunfield, K., and Wagner-Riddle, C. (2010). Soil microbial communities associated with nitrous oxide fluxes are affected by seasonal variation and tillage system. *In* "ASA, CSSA, and SSSA 2010 International Annual Meeting," http://a-c-s.confex.com/crops/2010am/webprogram/Paper60779.htmlLong Beach, CA, Oct. 31–Nov. 4. (last accessed Nov. 15, 2010).

Dunn, B. W., Batten, G. D., Beecher, H. G., and Ciavarella, S. (2002). The potential of near-infrared reflectance spectroscopy for soil analysis—A case study from the Riverine Plain of south-eastern Australia. *Aust. J. Exp. Agric.* **42,** 607–614.

Duxbury, J. M., Lauren, J. G., and Fruci, J. R. (1991). Measurement of the biologically active soil nitrogen fraction by a ^{15}N technique. *Agric. Ecosyst. Environ.* **34,** 121–129.

Ekenler, M., and Tabatabai, M. A. (2002). ß-Glucosaminidase activity of soils: Effect of cropping systems and its relationship to nitrogen mineralization. *Biol. Fertil. Soils* **36,** 367–376.

Elmi, A., Madramootoo, C., Hamel, C., and Liu, A. (2003). Denitrification and nitrous oxide to nitrous oxide plus dinitrogen ratios in the soil profile under three tillage systems. *Biol. Fertil. Soils* **38,** 340–348.

Fageria, N. K., and Baligar, V. C. (2005). Enhancing nitrogen use efficiency in crop plants. *Adv. Agron.* **88,** 97–185.

Firestone, M. K., and Davidson, E. A. (1989). Microbiological basis of NO and N_2O production and consumption in soil. *In* "Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere" (M. O. Andreae and D. S. Schimel, Eds.), pp. 7–21. Wiley, Berlin, Germany.

Fox, R. H., and Piekielek, W. P. (1978a). Field testing of several nitrogen availability indexes. *Soil Sci. Soc. Am. J.* **42,** 747–750.

Fox, R. H., and Piekielek, W. P. (1978b). A rapid method for estimating the nitrogen-supplying capability of a soil. *Soil Sci. Soc. Am. J.* **42,** 751–753.

Fox, R. H., Roth, G. W., Iversen, K. V., and Piekielek, W. P. (1989). Soil and tissue nitrate tests compared for predicting soil nitrogen availability to corn. *Agron. J.* **81,** 971–974.

Fox, R. H., Shenk, J. S., Piekielek, W. P., Westerhaus, M. O., Toth, J. D., and Macneal, K. E. (1993). Comparison of near-infrared spectroscopy and other soil nitrogen availability quick tests for corn. *Agron. J.* **85,** 1049–1053.

Franzluebbers, A. J., and Stuedemann, J. A. (2003). Bermudagrass management in the southern piedmont USA. III. Particulate and biologically active soil carbon. *Soil Sci. Soc. Am. J.* **67,** 132–138.

Franzluebbers, A. J., and Stuedemann, J. A. (2008). Early response of soil organic fractions to tillage and integrated crop-livestock production. *Soil Sci. Soc. Am. J.* **72,** 613–625.

Franzluebbers, A. J., Haney, R. L., Honeycutt, C. W., Schomberg, H. H., and Hons, F. M. (2000). Flush of carbon dioxide following rewetting of dried soil relates to active organic pools. *Soil Sci. Soc. Am. J.* **64,** 613–623.

Franzluebbers, A. J., Haney, R. L., Honeycutt, C. W., Arshad, M. A., Schomberg, H. H., and Hons, F. M. (2001). Climatic influences on active fractions of soil organic matter. *Soil Biol. Biochem.* **33,** 1103–1111.

Fuller, K. D., Gordon, R., Grimmett, M., Fillmore, S., Madani, A., VanRoestel, J., Stratton, G. W., MacLeod, J., Embree, C., and George, E. S. (2010). Seasonal and crop rotational effects of manure management on nitrate-nitrogen leaching in Nova Scotia. *Agric. Ecosyst. Environ.* **137,** 267–275.

Gagnon, B., and Ziadi, N. (2010). Grain corn and soil nitrogen responses to sidedress nitrogen sources and applications. *Agron. J.* **102,** 1014–1022.

Galvez-Sola, L., Moral, R., Moreno-Caselles, J., Perez-Murcia, M. D., Perez-Espinosa, A., Bustamante, M. A., and Paredes, C. (2009). Effectiveness of near infrared reflectance spectroscopy in the quick evaluation of nitrogen content in wewage sludge. *Commun. Soil Sci. Plant Anal.* **40,** 726–735.

Gianello, C., and Bremner, J. M. (1986a). Comparison of chemical methods of assessing potentially available organic nitrogen in soil. *Commun. Soil Sci. Plant Anal.* **17,** 215–236.

Gianello, C., and Bremner, J. M. (1986b). A simple chemical method of assessing potentially available organic nitrogen in soil. *Commun. Soil Sci. Plant Anal.* **17,** 195–214.

Gianello, C., and Bremner, J. M. (1988). A rapid steam distillation method of assessing potentially available organic nitrogen in soil. *Commun. Soil Sci. Plant Anal.* **19,** 1551–1568.

Gleeson, D. B., Müller, C., Banerjee, S., Ma, W., Siciliano, S. D., and Murphy, D. V. (2010). Response of ammonia oxidizing archaea and bacteria to changing water filled pore space. *Soil Biol. Biochem.* **42,** 1888–1891.

Graham, P. H. (2005). Biological dinitrogen fixation: Symbiotic. *In* "Principles and Applications of Soil Microbiology" (D. M. Sylvia, J. J. Fuhrmann, P. G. Hartel, and D. A. Zuberer, Eds.), pp. 405–432. Pearson Prentice Hall, Upper Saddle River, NJ.

Green, C. J., Blackmer, A. M., and Horton, R. (1995). Nitrogen effects on conservation of carbon during corn residue decomposition in soil. *Soil Sci. Soc. Am. J.* **59,** 453–459.

Gregorich, E. G., and Beare, M. H. (2008). Physically uncomplexed organic matter. *In* "Soil Sampling and Methods of Analysis" (M. R. Carter and E. G. Gregorich, Eds.), pp. 607–616. CRC Press, Boca Raton, FL, USA.

Gregorich, E. G., Carter, M. R., Angers, D. A., Monreal, C. M., and Ellert, B. H. (1994). Towards a minimum data set to assess soil organic matter quality in agricultural soils. *Can. J. Soil Sci.* **74,** 367–385.

Gregorich, E. G., Rochette, P., VandenBygaart, A. J., and Angers, D. A. (2005). Greenhouse gas contributions of agricultural soils and potential mitigation practices in eastern Canada. *Soil Tillage Res.* **83,** 53–72.

Gregorich, E. G., Beare, M. H., McKim, U. F., and Skjemstad, J. O. (2006a). Chemical and biological characteristics of physically uncomplexed organic matter. *Soil Sci. Soc. Am. J.* **70,** 975–985.

Gregorich, E. G., Rochette, P., Hopkins, D. W., McKim, U. F., and St-Georges, P. (2006b). Tillage-induced environmental conditions in soil and substrate limitation determine biogenic gas production. *Soil Biol. Biochem.* **38,** 2614–2628.

Gregorich, E. G., Rochette, P., VandenBygaart, A. J., and Angers, D. A. (2007). Corrigendum to "Greenhouse gas contributions of agricultural soils and potential mitigation practices in eastern Canada". [*Soil Tillage Res.* 83 (2005) 53–72] *Soil Tillage Res.* **94,** 262–263.

Gregorich, E. G., Rochette, P., St-Georges, P., McKim, U. F., and Chan, C. (2008). Tillage effects on N_2O emission from soils under corn and soybeans in eastern Canada. *Can. J. Soil Sci.* **88,** 153–161.

Griffin, T. S. (2008). Nitrogen availability. *In* "Nitrogen in Agricultural Systems. Agronomy Monograph 49" (J. S. Schepers and W. R. Raun, Eds.), pp. 613–646. ASA, CSSA, and SSSA, Madison, WI.

Griffin, T. S., and Honeycutt, C. W. (2000). Using growing degree days to predict nitrogen availability from livestock manures. *Soil Sci. Soc. Am. J.* **64,** 1876–1882.

Griffin, G. F., and Laine, A. F. (1983). Nitrogen mineralization in soils previously amended with organic wastes. *Agron. J.* **75,** 124–129.

Griffin, T. S., and Porter, G. A. (2004). Altering soil carbon and nitrogen stocks in intensively tilled two-year rotations. *Biol. Fertil. Soils* **39,** 366–374.

Halpern, M. T., Whalen, J. K., and Madramootoo, C. A. (2010). Long-term tillage and residue management influences soil carbon and nitrogen dynamics. *Soil Sci. Soc. Am. J.* **74,** 1211–1217.

Halvorson, A. D., and Reule, C. A. (2006). Irrigated corn and soybean response to nitrogen under no-till in northern Colorado. *Agron. J.* **98,** 1367–1374.

Hart, S. C., Stark, J. M., Davidson, E. A., and Firestone, M. K. (1994). Nitrogen mineralization, immobilization, and nitrification. *In* "Methods of Soil Analysis. Part 2. Microbiological and Biochemical Properties" (R. W. Weaver, S. Angle, P. Bottomley, D. Bezdicek, S. Smith, A. Tabatabai, and A. Wollum, Eds.), pp. 985–1018. SSSA, Madison, WI.

Hartel, P. G. (2005). The soil habitat. *In* "Principles and Applications of Soil Microbiology" (D. M. Sylvia, J. J. Fuhrmann, P. G. Hartel, and D. A. Zuberer, Eds.), pp. 26–53. Pearson Prentice Hall, Upper Saddle River, NJ.

Hartz, T. K., Bendixen, W. E., and Wierdsma, L. (2000). The value of presidedress soil nitrate testing as a nitrogen management tool in irrigated vegetable production. *HortScience* **35,** 651–656.

Hassink, J., Bouwman, L. A., Zwart, K. B., and Brussaard, L. (1993). Relationships between habitable pore space, soil biota and mineralization rates in grassland soils. *Soil Biol. Biochem.* **25,** 47–55.

Haynes, R. J. (1986). The decomposition process: Mineralization, immobilization, humus formation, and degradation. *In* "Mineral Nitrogen in the Plant-Soil System" (T. T. Kozlowski, Ed.), pp. 52–126. Academic Press, Inc., Orlando, FL.

Haynes, R. J. (2005). Labile organic matter fractions as central components of the quality of agricultural soils: An overview. *Adv. Agron.* **85,** 221–268.

Heckman, J. R., Hlubik, W. T., Prostak, D. J., and Paterson, J. W. (1995). Pre-sidedress soil nitrate test for sweet corn. *HortScience* **30,** 1033–1036.

Heckman, J. R., Morris, T., Sims, J. T., Sieczka, J. B., Krogmann, U., Nitzsche, P., and Ashley, R. (2002). Pre-sidedress soil nitrate test is effective for fall cabbage. *HortScience* **37,** 113–117.

Helgason, B., Janzen, H., Chantigny, M., Drury, C., Ellert, B., Gregorich, E., Lemke, R., Pattey, E., Rochette, P., and Wagner-Riddle, C. (2005). Toward improved coefficients for predicting direct N_2O emissions from soil in Canadian agroecosystems. *Nutr. Cycl. Agroecosyst.* **72,** 87–99.

Henriksen, T. M., and Breland, T. A. (1999). Nitrogen availability effects on carbon mineralization, fungal and bacterial growth, and enzyme activities during decomposition of wheat straw in soil. *Soil Biol. Biochem.* **31,** 1121–1134.

Herridge, D. F., Peoples, M. B., and Boddey, R. M. (2008). Global inputs of biological nitrogen fixation in agricultural systems. *Plant Soil* **311,** 1–18.

Holford, I. C. R., and Doyle, A. D. (1992). Yield responses and nitrogen fertilizer requirements of wheat in relation to soil nitratelevels at various depths. *Aust. J. Soil Res.* **30,** 683–694.

Holmes, W. E., and Zak, D. R. (1994). Soil microbial biomass dynamics and net nitrogen mineralization in northern hardwood ecosystems. *Soil Sci. Soc. Am. J.* **58,** 238–243.
Hong, S., Fox, R., and Piekielek, W. (1990). Field evaluation of several chemical indexes of soil nitrogen availability. *Plant Soil* **123,** 83–88.
Hooker, K. V., Coxon, C. E., Hackett, R., Kirwan, L. E., O'Keeffe, E., and Richards, K. G. (2008). Evaluation of cover crop and reduced cultivation for reducing nitrate leaching in Ireland. *J. Environ. Qual.* **37,** 138–145.
Hu, C., and Cao, Z. (2007). Size and activity of the soil microbial biomass and soil enzyme activity in long-term field experiments. *World J. Agric. Sci.* **3,** 63–70.
Jalil, A., Campbell, C. A., Jame, Y. W., Schoenau, J., Henry, J. L., and Lafond, G. P. (1996). Assessment of two chemical extraction methods as indices of available nitrogen. *Soil Sci. Soc. Am. J.* **60,** 1954–1960.
Janzen, H. H., Campbell, C. A., Brandt, S. A., Lafond, G. P., and Townley-Smith, L. (1992). Light-fraction organic matter in soils from long-term crop rotations. *Soil Sci. Soc. Am. J.* **56,** 1799–1806.
Janzen, H. H., Beauchemin, K. A., Bruinsma, Y., Campbell, C. A., Desjardins, R. L., Ellert, B. H., and Smith, E. G. (2003). The fate of nitrogen in agroecosystems: An illustration using Canadian estimates. *Nutr. Cycl. Agroecosyst.* **67,** 85–102.
Jones, D. L., Shannon, D., Junvee-Fortune, T., and Farrar, J. F. (2005). Plant capture of free amino acids is maximized under high soil amino acid concentrations. *Soil Biol. Biochem.* **37,** 179–181.
Kaharabata, S. K., Drury, C. F., Priesack, E., Desjardins, R. L., McKenney, D. J., Tan, C. S., and Reynolds, D. (2003). Comparing measured and expert-N predicted N_2O emissions from conventional till and no till corn treatments. *Nutr. Cycl. Agroecosyst.* **66,** 107–118.
Kay, B. D., Mahboubi, A. A., Beauchamp, E. G., and Dharmakeerthi, R. S. (2006). Integrating soil and weather data to describe variability in plant available nitrogen. *Soil Sci. Soc. Am. J.* **70,** 1210–1221.
Kemmitt, S. J., Lanyon, C. V., Waite, I. S., Wen, Q., Addiscott, T. M., Bird, N. R. A., O'Donnell, A. G., and Brookes, P. C. (2008). Mineralization of native soil organic matter is not regulated by the size, activity or composition of the soil microbial biomass—A new perspective. *Soil Biol. Biochem.* **40,** 61–73.
Khan, S. A., Mulvaney, R. L., and Hoeft, R. G. (2001). A simple soil test for detecting sites that are nonresponsive to nitrogen fertilization. *Soil Sci. Soc. Am. J.* **65,** 1751–1760.
Khorsandi, N., and Nourbakhsh, F. (2007). Effect of amendment of manure and corn residues on soil N mineralization and enzyme activity. *Agron. Sustainable Dev.* **27,** 139–143.
Klapwyk, J. H., and Ketterings, Q. M. (2006). Soil tests for predicting corn response to nitrogen fertilizer in New York. *Agron. J.* **98,** 675–681.
Klapwyk, J. H., Ketterings, Q. M., Godwin, G. S., and Wang, D. (2006). Response of the Illinois soil nitrogen test to liquid and composted dairy manure applications in a corn agroecosystem. *Can. J. Soil Sci.* **86,** 655–663.
Klausner, S. D., Reid, W. S., and Bouldin, D. R. (1993). Relationship between late spring soil nitrate concentrations and corn yields in New York. *J. Prod. Agric.* **6,** 350–354.
Kleber, M. (2010). What is recalcitrant soil organic matter? *Environ. Chem.* **7,** 320–332.
Knicker, H. (2000). Biogenic nitrogen in soils as revealed by solid-state carbon-13 and nitrogen-15 nuclear magnetic resonance spectroscopy. *J. Environ. Qual.* **29,** 715–723.
Knicker, H. (2004). Stabilization of N-compounds in soil and organic-matter-rich sediments - What is the difference? *Mar. Chem.* **92,** 167–195.
Knicker, H., and Hatcher, P. G. (1997). Survival of protein in an organic-rich sediment: Possible protection by encapsulation in organic matter. *Naturwissenschaften* **84,** 231–234.
Kolberg, R. L., Westfall, D. G., and Peterson, G. A. (1999). Influence of cropping intensity and nitrogen fertilizer rates on in situ nitrogen mineralization. *Soil Sci. Soc. Am. J.* **63,** 129–134.

Kuzyakov, Y., Blagodatskaya, E., and Blagodatsky, S. (2009). Comments on the paper by Kemmitt *et al.* (2008) 'Mineralization of native soil organic matter is not regulated by the size, activity or composition of the soil microbial biomass - A new perspective. [*Soil Biol. Biochem.* **40,** 61–73]: The biology of the Regulatory Gate. *Soil Biol. Biochem.* **41,** 435–439.
Laboski, C. A. M., Sawyer, J. E., Walters, D. T., Bundy, L. G., Hoeft, R. G., Randall, G. W., and Andraski, T. W. (2008). Evaluation of the Illinois soil nitrogen test in the north central region of the United States. *Agron. J.* **100,** 1070–1076.
Laungani, R., and Knops, J. (2009). Indirect plant species impacts on gross nitrogen mineralization in grasslands. *In* "94th ESA Annual Meeting," http://eco.confex.com/eco/2009/techprogram/P17930.HTM, 2–7 August, 2009. Albuquerque, NM. (last accessed Oct. 20, 2010).
Liang, B. C., and MacKenzie, A. F. (1996). Effect of fertilization on organic and microbial biomass nitrogen using ^{15}N under corn (*Zea mays* L.) in two Québec soils. *Fert. Res.* **44,** 143–149.
Liang, C., Zhang, X., and Balser, T. C. (2007a). Net microbial amino sugar accumulation process in soil as influenced by different plant material inputs. *Biol. Fertil. Soils* **44,** 1–7.
Liang, C., Zhang, X., Rubert Iv, K. F., and Balser, T. C. (2007b). Effect of plant materials on microbial transformation of amino sugars in three soil microcosms. *Biol. Fertil. Soils* **43,** 631–639.
Ma, B. L., Dwyer, L. M., and Gregorich, E. G. (1999). Soil nitrogen amendment effects on seasonal nitrogen mineralization and nitrogen cycling in maize production. *Agron. J.* **91,** 1003–1009.
Ma, B. L., Subedi, K. D., and Zhang, T. Q. (2007). Pre-sidedress nitrate test and other crop-based indicators for fresh market and processing sweet corn. *Agron. J.* **99,** 174–183.
Maclean, A. A. (1964). Measurement of nitrogen supplying-power of soils by extraction with sodium bicarbonate. *Nature* **203,** 1307–1308.
Magdoff, F. R., Ross, D., and Amadon, J. (1984). A soil test for nitrogen availability to corn. *Soil Sci. Soc. Am. J.* **48,** 1301–1304.
Mahmood, T., Kaiser, W., Ali, R., Ashraf, M., Gulnaz, A., and Iqbal, Z. (2005). Ammonium and nitrate nutrition of plants stimulates microbial activity in the rhizosphere. *Plant Soil* **277,** 233–243.
Malhi, S. S., and McGill, W. B. (1982). Nitrification in three Alberta soils: Effect of temperature, moisture and substrate concentration. *Soil Biol. Biochem.* **14,** 393–399.
Malhi, S. S., and Nyborg, M. (1988). Control of nitrification of fertilizer nitrogen: Effect of inhibitors, banding and nesting. *Plant Soil* **107,** 245–250.
Malley, D. F., Yesmin, L., Wray, D., and Edwards, S. (1999). Application of near-infrared spectroscopy in analysis of soil mineral nutrients. *Commun. Soil Sci. Plant Anal.* **30,** 999–1012.
Malley, D. F., Yesmin, L., and Eilers, R. G. (2002). Rapid analysis of hog manure and manure-amended soils using near-infrared spectroscopy. *Soil Sci. Soc. Am. J.* **66,** 1677–1686.
Marriott, E. E., and Wander, M. M. (2006). Total and labile soil organic matter in organic and conventional farming systems. *Soil Sci. Soc. Am. J.* **70,** 950–959.
Marschner, P., Yang, C. H., Lieberei, R., and Crowley, D. E. (2001). Soil and plant specific effects on bacterial community composition in the rhizosphere. *Soil Biol. Biochem.* **33,** 1437–1445.
Martin, P. D., Malley, D. F., Manning, G., and Fuller, L. (2002). Determination of soil organic carbon and nitrogen at the field level using near-infrared spectroscopy. *Can. J. Soil Sci.* **82,** 413–422.
McTaggart, I. P., and Smith, K. A. (1993). Estimation of potentially mineralisable nitrogen in soil by KCl extraction. *Plant Soil* **157,** 175–184.

Mikha, M. M., and Rice, C. W. (2004). Tillage and manure effects on soil and aggregate-associated carbon and nitrogen. *Soil Sci. Soc. Am. J.* **68,** 809–816.

Mikha, M. M., Rice, C. W., and Milliken, G. A. (2005). Carbon and nitrogen mineralization as affected by drying and wetting cycles. *Soil Biol. Biochem.* **37,** 339–347.

Mikha, M. M., Rice, C. W., and Benjamin, J. G. (2006). Estimating soil mineralizable nitrogen under different management practices. *Soil Sci. Soc. Am. J.* **70,** 1522–1531.

Miller, A. E., Schimel, J. P., Meixner, T., Sickman, J. O., and Melack, J. M. (2005). Episodic rewetting enhances carbon and nitrogen release from chaparral soils. *Soil Biol. Biochem.* **37,** 2195–2204.

Miller, M. N., Zebarth, B. J., Dandie, C. E., Burton, D. L., Goyer, C., and Trevors, J. T. (2008). Crop residue influence on denitrification, N_2O emissions and denitrifier community abundance in soil. *Soil Biol. Biochem.* **40,** 2553–2562.

Mkhabela, M. S., Madani, A., Gordon, R., Burton, D., Cudmore, D., Elmi, A., and Hart, W. (2008). Gaseous and leaching nitrogen losses from no-tillage and conventional tillage systems following surface application of cattle manure. *Soil Tillage Res.* **98,** 187–199.

Mosier, A. R. (1998). Soil processes and global change. *Biol. Fertil. Soils* **27,** 221–229.

Mosier, A. R. (2001). Exchange of gaseous nitrogen compounds between agricultural systems and the atmosphere. *Plant Soil* **228,** 17–27.

Mueller, T., and Thorup-Kristensen, K. (2001). N-fixation of selected green manure plants in an organic crop rotation. *Biol. Agric. Hort.* **18,** 345–363.

Mulvaney, R. L., Khan, S. A., Hoeft, R. G., and Brown, H. M. (2001). A soil organic nitrogen fraction that reduces the need for nitrogen fertilization. *Soil Sci. Soc. Am. J.* **65,** 1164–1172.

Mulvaney, R. L., Khan, S. A., and Ellsworth, T. R. (2006). Need for a soil-based approach in managing nitrogen fertilizers for profitable corn production. *Soil Sci. Soc. Am. J.* **70,** 172–182.

Muruganandam, S., Israel, D. W., and Robarge, W. P. (2009). Activities of nitrogen-mineralization enzymes associated with soil aggregate size fractions of three tillage systems. *Soil Sci. Soc. Am. J.* **73,** 751–759.

Muruganandam, S., Israel, D. W., and Robarge, W. P. (2010). Nitrogen transformations and microbial communities in soil aggregates from three tillage systems. *Soil Sci. Soc. Am. J.* **74,** 120–129.

Myrold, D. D. (2005). Transformations of nitrogen. *In* "Principles and Applications of Soil Microbiology" (D. M. Sylvia, J. J. Fuhrmann, P. G. Hartel, and D. A. Zuberer, Eds.), pp. 333–372. Pearson Prentice Hall, Upper Saddle River, NJ.

Myrold, D. D., and Bottomley, P. P. (2008). Nitrogen mineralization and immobilization. *In* "Nitrogen in Agricultural Systems" (J. S. Schepers and W. R. Raun, Eds.), pp. 157–172. ASA, CSSA, SSSA, Madison, WI.

Nannipieri, P., Ascher, J., Ceccherini, M. T., Landi, L., Pietramellara, G., Renella, G., and Valori, F. (2008). Effects of root exudates in microbial diversity and activity in rhizosphere soils. *In* "Molecular Mechanisms of Plant and Microbe Coexistence" (C. S. Nautiyal and P. Dion, Eds.), pp. 339–365. Springer, Berlin, Germany.

Nduwamungu, C., Ziadi, N., Parent, L. É., Tremblay, G. F., and Thuriès, L. (2009a). Opportunities for, and limitations of, near infrared reflectance spectroscopy applications in soil analysis: A review. *Can. J. Soil Sci.* **89,** 531–541.

Nduwamungu, C., Ziadi, N., Tremblay, G. F., and Parent, L.-E. (2009b). Near-infrared reflectance spectroscopy prediction of soil properties: Effects of sample cups and preparation. *Soil Sci. Soc. Am. J.* **73,** 1896–1903.

Nicol, G. W., Leininger, S., Schleper, C., and Prosser, J. I. (2008). The influence of soil pH on the diversity, abundance and transcriptional activity of ammonia oxidizing archaea and bacteria. *Environ. Microbiol.* **10,** 2966–2978.

Nyiraneza, J., N'Dayegamiye, A., Chantigny, M. H., and Laverdiere, M. R. (2009). Variations in corn yield and nitrogen uptake in relation to soil attributes and nitrogen availability indices. *Soil Sci. Soc. Am. J.* **73,** 317–327.

O'Halloran, I. P., von Bertoldi, A. P., and Peterson, S. (2004). Spatial variability of barley (*Hordeum vulgare*) and corn (*Zea mays* L.) yields, yield response to fertilizer N and soil N test levels. *Can. J. Soil Sci.* **84,** 307–316.

Olk, D. C. (2008a). Organic forms of nitrogen. *In* "Soil Sampling and Methods of Analysis" (M. R. Carter and E. G. Gregorich, Eds.), 2nd edn., pp. 667–674. CRC Press, Boca Raton, Fl.

Olk, D. C. (2008b). Organic forms of soil nitrogen. Agronomy Monograph 49. *In* "Nitrogen in Agricultural Systems" (J. S. Schepers and W. R. Raun, Eds.), pp. 57–100. ASA, CSSA, SSSA, Madison, WI.

Parkin, T. B., Kaspar, T. C., and Cambardella, C. (2002). Oat plant effects on net nitrogen mineralization. *Plant Soil* **243,** 187–195.

Pathak, H., and Rao, D. L. N. (1998). Carbon and nitrogen mineralization from added organic matter in saline and alkali soils. *Soil Biol. Biochem.* **30,** 695–702.

Patni, N. K., Masse, L., and Jui, P. Y. (1998). Groundwater quality under conventional and no tillage: I. Nitrate, electrical conductivity, and pH. *J. Environ. Qual.* **27,** 869–877.

Patra, D. D., Brookes, P. C., Coleman, K., and Jenkinson, D. S. (1990). Seasonal changes of soil microbial biomass in an arable and a grassland soil which have been under uniform management for many years. *Soil Biol. Biochem.* **22,** 739–742.

Paul, J. W., and Zebarth, B. J. (1997a). Denitrification and nitrate leaching during the fall and winter following dairy cattle slurry application. *Can. J. Soil Sci.* **77,** 231–240.

Paul, J. W., and Zebarth, B. J. (1997b). Denitrification during the growing season following dairy cattle slurry and fertilizer applicatio for silage corn. *Can. J. Soil Sci.* **77,** 241–248.

Paul, K. I., Polglase, P. J., O'Connell, A. M., Carlyle, J. C., Smethurst, P. J., and Khanna, P. K. (2003). Defining the relation between soil water content and net nitrogen mineralization. *Eur. J. Soil Sci.* **54,** 39–48.

Pelletier, F., Prévost, D., Laliberté, G., and Van Bochove, E. (1999). Seasonal response of denitrifiers to temperature in a Quebec cropped soil. *Can. J. Soil Sci.* **79,** 551–556.

Petersen, S. O., Schjønning, P., Thomsen, I. K., and Christensen, B. T. (2008). Nitrous oxide evolution from structurally intact soil as influenced by tillage and soil water content. *Soil Biol. Biochem.* **40,** 967–977.

Phillips, R. L. (2007). Organic agriculture and nitrous oxide emissions at sub-zero soil temperatures. *J. Environ. Qual.* **36,** 23–30.

Phillips, R. L. (2008). Denitrification in cropping systems at sub-zero soil temperatures. A review. *Agron. Sustainable Dev.* **28,** 87–93.

Picone, L. I., Cabrera, M. L., and Franzluebbers, A. J. (2002). A rapid method to estimate potentially mineralizable nitrogen in soil. *Soil Sci. Soc. Am. J.* **66,** 1843–1847.

Postma-Blaauw, M. B., de Vries, F. T., de Goede, R. G. M., Bloem, J., Faber, J. H., and Brussaard, L. (2005). Within-trophic group interactions of bacterivorous nematode species and their effects on the bacterial community and nitrogen mineralization. *Oecologia* **142,** 428–439.

Postma-Blaauw, M. B., Bloem, J., Faber, J. H., van Groenigen, J. W., de Goede, R. G. M., and Brussaard, L. (2006). Earthworm species composition affects the soil bacterial community and net nitrogen mineralization. *Pedobiologia* **50,** 243–256.

Puri, G., and Ashman, M. R. (1998). Relationship between soil microbial biomass and gross N mineralisation. *Soil Biol. Biochem.* **30,** 251–256.

Qian, P., and Schoenau, J. J. (1995). Assessing nitrogen mineralization from soil organic matter using anion exchange membranes. *Nutr. Cycling Agroecosyst.* **40,** 143–148.

Qian, P., and Schoenau, J. J. (2002). Practical applications of ion exchange resins in agricultural and environmental soil research. *Can. J. Soil Sci.* **82,** 9–21.

Qian, P., and Schoenau, J. J. (2005). Use of ion-exchange membrane to assess nitrogen-supply power of soils. *J. Plant Nutr.* **28,** 2193–2200.

Qian, P., Schoenau, J. J., and Huang, W. Z. (1992). Use of ion exchange membranes in routine soil testing. *Commun. Soil Sci. Plant Anal.* **23,** 1791–1804.

Redl, G., Hübner, C., and Wurst, F. (1990). Changes in hot water soil extracts brought about by nitrogen immobilization and mineralization processes during incubation of amended soils. *Biol. Fertil. Soils* **10,** 45–49.

Reeves, J. B. III., and Van Kessel, J. S. (2000). Near-infrared spectroscopic determination of carbon, total nitrogen, and ammonium-N in dairy manures. *J. Dairy Sci.* **83,** 1829–1836.

Richardson, D., Felgate, H., Watmough, N., Thomson, A., and Baggs, E. (2009). Mitigating release of the potent greenhouse gas N_2O from the nitrogen cycle—Could enzymic regulation hold the key? *Trends Biotechnol.* **27,** 388–397.

Riedell, W. E., Pikul, J. L. Jr., Jaradat, A. A., and Schumacher, T. E. (2009). Crop rotation and nitrogen input effects on soil fertility, maize mineral nutrition, yield, and seed composition. *Agron. J.* **101,** 870–879.

Robinson, J. B. D. (1967). Anaerobic incubation of soil and the production of ammonium. *Nature* **214,** 534.

Rochette, P., van Bochove, E., Prevost, D., Angers, D. A., Cote, D., and Bertrand, N. (2000). Soil carbon and nitrogen dynamics following application of pig slurry for the 19th consecutive year: II. Nitrous oxide fluxes and mineral nitrogen. *Soil Sci. Soc. Am. J.* **64,** 1396–1403.

Rochette, P., Angers, D. A., Chantigny, M. H., MacDonald, J. D., Gasser, M. O., and Bertrand, N. (2009). Reducing ammonia volatilization in a no-till soil by incorporating urea and pig slurry in shallow bands. *Nutr. Cycl. Agroecosyst.* **84,** 71–80.

Rovira, P., Kurz-Besson, C., Hernàndez, P., Coûteaux, M. M., and Vallejo, V. R. (2008). Searching for an indicator of N evolution during organic matter decomposition based on amino acids behaviour: A study on litter layers of pine forests. *Plant Soil* **307,** 149–166.

Sahrawat, K. L. (2008). Factors affecting nitrification in soils. *Commun. Soil Sci. Plant Anal.* **39,** 1436–1446.

Sanchez, J. E., Harwood, R. R., Willson, T. C., Kizilkaya, K., Smeenk, J., Parker, E., Paul, E. A., Knezek, B. D., and Robertson, G. P. (2004). Managing soil carbon and nitrogen for productivity and environmental quality. *Agron. J.* **96,** 769–775.

Sauheitl, L., Glaser, B., and Weigelt, A. (2009). Uptake of intact amino acids by plants depends on soil amino acid concentrations. *Environ. Exp. Bot.* **66,** 145–152.

Savin, M. C., Görres, J. H., Neher, D. A., and Amador, J. A. (2001). Biogeophysical factors influencing soil respiration and mineral nitrogen content in an old field soil. *Soil Biol. Biochem.* **33,** 429–438.

Savin, M. C., Görres, J. H., and Amador, J. A. (2004). Microbial and Microfaunal Community Dynamics in Artificial and (L.) Burrows. Soil Sci.*Soc. Am. J.* **68,** 116–124.

Schepers, J. S., and Meisinger, J. J. (1994). Field indicators of nitrogen mineralization. *In* "Soil Testing: Prospects for Improving Nutrient Recommendations" (J. L. Havlin and J. S. Jacobsen, Eds.), pp. 31–47. SSSA, ASA, Madison, WI.

Schnürer, J., Clarholm, M., and Rosswall, T. (1985). Microbial biomass and activity in an agricultural soil with different organic matter contents. *Soil Biol. Biochem.* **17,** 611–618.

Schomberg, H. H., Wietholter, S., Griffin, T. S., Reeves, D. W., Cabrera, M. L., Fisher, D. S., Endale, D. M., Novak, J. M., Balkcom, K. S., Raper, R. L., Kitchen, N. R., Locke, M. A., *et al.* (2009). Assessing indices for predicting potential nitrogen mineralization in soils under different management systems. *Soil Sci. Soc. Am. J.* **73,** 1575–1586.

Serna, M. D., and Pomares, F. (1992). Evaluation of chemical indices of soil organic nitrogen availability in calcareous soils. *Soil Sci. Soc. Am. J.* **56,** 1486–1491.

Sey, B. K., Whalen, J. K., Gregorich, E. G., Rochette, P., and Cue, R. I. (2008). Carbon dioxide and nitrous oxide content in soils under corn and soybean. *Soil Sci. Soc. Am. J.* **72,** 931–938.

Sharifi, M., Zebarth, B., Burton, D., Grant, C., Porter, G., Cooper, J., Leclerc, Y., Moreau, G., and Arsenault, W. (2007a). Evaluation of laboratory-based measures of soil mineral nitrogen and potentially mineralizable nitrogen as predictors of field-based indices of soil nitrogen supply in potato production. *Plant Soil* **301,** 203–214.

Sharifi, M., Zebarth, B. J., Burton, D. L., Grant, C. A., and Cooper, J. M. (2007b). Evaluation of some indices of potentially mineralizable nitrogen in soil. *Soil Sci. Soc. Am. J.* **71,** 1233–1239.

Sharifi, M., Zebarth, B. J., Burton, D. L., Grant, C. A., Bittman, S., Drury, C. F., McConkey, B. G., and Ziadi, N. (2008a). Response of potentially mineralizable soil nitrogen and indices of nitrogen availability to tillage system. *Soil Sci. Soc. Am. J.* **72,** 1124–1131.

Sharifi, M., Zebarth, B. J., Burton, D. L., Grant, C. A., and Porter, G. A. (2008b). Organic amendment history and crop rotation effects on soil nitrogen mineralization potential and soil nitrogen supply in a potato cropping system. *Agron. J.* **100,** 1562–1572.

Sharifi, M., Lynch, D., Zebarth, B., Zheng, Z., and Martin, R. (2009a). Evaluation of nitrogen supply rate measured by in situ placement of plant root simulator™ probes as a predictor of nitrogen supply from soil and organic amendments in potato crop. *Am. J. Potato Res.* **86,** 356–366.

Sharifi, M., Zebarth, B. J., Burton, D. L., Grant, C. A., Hajabbasi, M. A., and Abbassi-Kalo, G. (2009b). Sodium hydroxide direct distillation: A method for estimating total nitrogen in soil. *Commun. Soil Sci. Plant Anal.* **40,** 2505–2520.

Sharifi, M., Zebarth, B. J., Porter, G. A., Burton, D. L., and Grant, C. A. (2009c). Soil mineralizable nitrogen and soil nitrogen supply under two-year potato rotations. *Plant Soil* **320,** 267–279.

Sierra, J. (1997). Temperature and soil moisture dependence of N mineralization in intact soil cores. *Soil Biol. Biochem.* **29,** 1557–1563.

Sierra, J. (2002). Nitrogen mineralization and nitrification in a tropical soil: Effects of fluctuating temperature conditions. *Soil Biol. Biochem.* **34,** 1219–1226.

Simard, R. R., and N'Dayegamiye, A. (1993). Nitrogen-mineralization potential of meadow soils. *Can. J. Soil Sci.* **73,** 27–38.

Simard, R. R., Angers, D. A., and Lapierre, C. (1994). Soil organic matter quality as influenced by tillage, lime, and phosphorus. *Biol. Fertil. Soils* **18,** 13–18.

Singh, B. K., Millard, P., Whiteley, A. S., and Murrell, J. C. (2004). Unravelling rhizosphere-microbial interactions: Opportunities and limitations. *Trends Microbiol.* **12,** 386–393.

Singh, B. K., Dawson, L. A., Macdonald, C. A., and Buckland, S. M. (2009). Impact of biotic and abiotic interaction on soil microbial communities and functions: A field study. *Appl. Soil Ecol.* **41,** 239–248.

Singurindy, O., Molodovskaya, M., Richards, B. K., and Steenhuis, T. S. (2009). Nitrous oxide emission at low temperatures from manure-amended soils under corn (*Zea mays* L.). Agric. *Ecosyst. Environ.* **132,** 74–81.

Six, J., Elliott, E. T., and Paustian, K. (1999). Aggregate and soil organic matter dynamics under conventional and no-tillage systems. *Soil Sci. Soc. Am. J.* **63,** 1350–1358.

Six, J., Conant, R. T., Paul, E. A., and Paustian, K. (2002). Stabilization mechanisms of soil organic matter: Implications for C-saturation of soils. *Plant Soil* **241,** 155–176.

Smil, V. (1999). Nitrogen in crop production: An account of global flows. *Glob. Biogeochem. Cycles* **13,** 647–662.

Smith, J. L., and Paul, E. A. (1990). The significance of soil microbial biomass estimations. *In* "Soil Biochemistry, Vol. 6" (J. M. Bollag and G. Stotzky, Eds.), pp. 357–396. Marcel Dekker, New York, NY.

Smith, K. A., and Li, S. (1993). Estimation of potentially mineralizable nitrogen in soil by KCl extraction. *Plant Soil* **157,** 167–174.

Smith, W. N., Grant, B., Desjardins, R. L., Lemke, R., and Li, C. (2004). Estimates of the interannual variations of N_2O emissions from agricultural soils in Canada. *Nutr. Cycl. Agroecosyst.* **68,** 37–45.

Song, Y. N., Marschner, P., Li, L., Bao, X. G., Sun, J. H., and Zhang, F. S. (2007). Community composition of ammonia-oxidizing bacteria in the rhizosphere of intercropped wheat (*Triticum aestivum* L.), maize (*Zea mays* L.), and faba bean (*Vicia faba* L.). *Biol. Fertil. Soils* **44,** 307–314.

Sorensen, L. K., and Dalsgaard, S. (2005). Determination of clay and other soil properties by near infrared spectroscopy. *Soil Sci. Soc. Am. J.* **69,** 159–167.

Stanford, G. (1978). Evaluation of ammonium release by alkaline permanganate extraction as an index of soil nitrogen availability. *Soil Sci.* **126,** 244–253.

Stanford, G., and Smith, S. J. (1972). Nitrogen mineralization potentials of soils. *Soil Sci. Soc. Am. J.* **36,** 465–472.

Stanford, G., Frere, M. H., and Schwaninger, D. H. (1973). Temperature coefficient of soil nitrogen mineralization. *Soil Sci.* **115,** 321–323.

Stanford, G., Frere, M. H., and Vander Pol, R. A. (1975). Effect of fluctuating temperatures on soil nitrogen mineralization. *Soil Sci.* **119,** 222–226.

Stanger, T. F., and Lauer, J. G. (2008). Corn grain yield response to crop rotation and nitrogen over 35 years. *Agron. J.* **100,** 643–650.

Stark, J. C., and Porter, G. A. (2005). Potato nutrient management in sustainable cropping systems. *Am. J. Potato Res.* **82,** 329–338.

Stevens, W. B., Hoeft, R. G., and Mulvaney, R. L. (2005). Fate of nitrogen-15 in a long-term nitrogen rate study. *Agron. J.* **97,** 1046–1053.

Stevenson, F. J. (1986). Cycles of Soil: Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients. John Wiley & Sons, New York.

Stoddard, C. S., Grove, J. H., Coyne, M. S., and Thom, W. O. (2005). Fertilizer, tillage, and dairy manure contributions to nitrate and herbicide leaching. *J. Environ. Qual.* **34,** 1354–1362.

Subbarao, G. V., Ito, O., Sahrawat, K. L., Berry, W. L., Nakahara, K., Ishikawa, T., Watanabe, T., Suenaga, K., Rondon, M., and Rao, I. M. (2006). Scope and strategies for regulation of nitrification in agricultural systems—Challenges and opportunities. *Crit. Rev. Plant Sci.* **25,** 303–335.

Subler, S., and Kirsch, A. S. (1998). Spring dynamics of soil carbon, nitrogen, and microbial activity in earthworm middens in a no-till cornfield. *Biol. Fertil. Soils* **26,** 243–249.

Subler, S., Blair, J. M., and Edwards, C. A. (1995). Using anion-exchange membranes to measure soil nitrate availability and net nitrification. *Soil Biol. Biochem.* **27,** 911–917.

Sudduth, K. A., and Hummel, J. W. (1993a). Portable, near-infrared spectrophotometer for rapid soil analysis. *Trans. Am. Soc. Agric. Eng.* **36,** 185–194.

Sudduth, K. A., and Hummel, J. W. (1993b). Soil organic matter, CEC, and moisture sensing with a portable NIR spectrophotometer. *Trans. Am. Soc. Agric. Eng.* **36,** 1571–1582.

Tan, C. S., Drury, C. F., Reynolds, W. D., Gaynor, J. D., Zhang, T. Q., and Ng, H. Y. (2002a). Effect of long-term conventional tillage and no-tillage systems on soil and water quality at the field scale. *Water Sci. Technol.* **46,** 183–190.

Tan, C. S., Drury, C. F., Reynolds, W. D., Groenevelt, P. H., and Dadfar, H. (2002b). Water and nitrate loss through tiles under a clay loam soil in Ontario after 42 years of consistent fertilization and crop rotation. *Agric. Ecosyst. Environ.* **93,** 121–130.

Tan, Z., Lal, R., Owens, L., and Izaurralde, R. C. (2007). Distribution of light and heavy fractions of soil organic carbon as related to land use and tillage practice. *Soil Tillage Res.* **92,** 53–59.

Tan, I. Y. S., van Es, H. M., Duxbury, J. M., Melkonian, J. J., Schindelbeck, R. R., Geohring, L. D., Hively, W. D., and Moebius, B. N. (2009). Single-event nitrous oxide losses under maize production as affected by soil type, tillage, rotation, and fertilization. *Soil Tillage Res.* **102,** 19–26.

Teepe, R., Brumme, R., and Beese, F. (2001). Nitrous oxide emissions from soil during freezing and thawing periods. *Soil Biol. Biochem.* **33,** 1269–1275.

Thorup-Kristensen, K., Magid, J., and Jensen, L. S. (2003). Catch crops and green manures as biological tools in nitrogen management in temperate zones. *Adv. Agron.* **79,** 227–302.

Tisdale, S. L., Nelson, W. L., and Beaton, J. D. (1985). Soil Fertility and Fertilizers. 4th edn., Macmillan Publishing Company, New York.

Treusch, A. H., Leininger, S., Kietzin, A., Schuster, S. C., Klenk, H. P., and Schleper, C. (2005). Novel genes for nitrite reductase and Amo-related proteins indicate a role of uncultivated mesophilic crenarchaeota in nitrogen cycling. *Environ. Microbiol.* **7,** 1985–1995.

Vance, E. D., Brookes, P. C., and Jenkinson, D. S. (1987). An extraction method for measuring soil microbial biomass C. *Soil Biol. Biochem.* **19,** 703–707.

Vanotti, M. B., Leclerc, S. A., and Bundy, L. G. (1995). Short-term effects of nitrogen fertilization on soil organic nitrogen availability. *Soil Sci. Soc. Am. J.* **59,** 1350–1359.

Vasques, G. M., Grunwald, S., and Sickman, J. O. (2009). Modeling of soil organic carbon fractions using visible-near-infrared spectroscopy. *Soil Sci. Soc. Am. J.* **73,** 176–184.

Velthof, G. L., Kuikman, P. J., and Oenema, O. (2003). Nitrous oxide emission from animal manures applied to soil under controlled conditions. *Biol. Fertil. Soils* **37,** 221–230.

Voroney, R. P., Brookes, P. C., and Beyaert, R. P. (2008). Soil microbial biomass C, N, P, and S. *In* "Soil Sampling and Methods of Soil Analysis" (M. R. Carter and E. G. Gregorich, Eds.), pp. 637–652. CRC Press, Boca Raton, FL.

Wagner-Riddle, C., Furon, A., McLaughlin, N. L., Lee, I., Barbeau, J., Jayasundara, S., Parkin, G., von Bertoldi, P., and Warland, J. (2007). Intensive measurement of nitrous oxide emissions from a corn-soybean-wheat rotation under two contrasting management systems over 5 years. *Glob. Change Biol.* **13,** 1722–1736.

Wang, W., Smith, C. J., Chalk, P. M., and Chen, D. (2001). Evaluating chemical and physical indices of nitrogen mineralization capacity with an unequivocal reference. *Soil Sci. Soc. Am. J.* **65,** 368–376.

Wang, W. J., Smith, C. J., and Chen, D. (2003). Towards a standardised procedure for determining the potentially mineralisable nitrogen of soil. *Biol. Fertil. Soils* **37,** 362–374.

Webb, J., Pain, B., Bittman, S., and Morgan, J. (2010). The impacts of manure application methods on emissions of ammonia, nitrous oxide and on crop response—A review. *Agric. Ecosyst. Environ.* **137,** 39–46.

Westerman, R. L., Boman, R. K., Raun, W. R., and Johnson, G. V. (1994). Ammonium and nitrate nitrogen in soil profiles of long-term winter wheat fertilization experiments. *Agron. J.* **86,** 94–99.

Wetselaar, R., Passioura, J. B., and Singh, B. R. (1972). Consequences of banding nitrogen fertilizers in soil—I. Effects on nitrification. *Plant Soil* **36,** 159–175.

Whalen, J. K., and Sampedro, L. (2010). Soil Ecology and Management. CAB International, UK.

Whalen, J. K., Bottomley, P. J., and Myrold, D. D. (2000). Carbon and nitrogen mineralization from light- and heavy-fraction additions to soil. *Soil Biol. Biochem.* **32,** 1345–1352.

Whalen, J., Chang, C., and Olson, B. (2001). Nitrogen and phosphorus mineralization potentials of soils receiving repeated annual cattle manure applications. *Biol. Fertil. Soils* **34,** 334–341.

Williams, P. H., Jarvis, S. C., and Dixon, E. (1998). Emission of nitric oxide and nitrous oxide from soil under field and laboratory conditions. *Soil Biol. Biochem.* **30,** 1885–1893.

Williams, J. D., Crozier, C. R., White, J. G., Heiniger, R. W., Sripada, R. P., and Crouse, D. A. (2007a). Illinois soil nitrogen test predicts southeastern U.S. corn economic optimum nitrogen rates. *Soil Sci. Soc. Am. J.* **71,** 735–744.

Williams, J. D., Crozier, C. R., White, J. G., Sripada, R. P., and Crouse, D. A. (2007b). Comparison of soil nitrogen tests for corn fertilizer recommendations in the humid southeastern USA. *Soil Sci. Soc. Am. J.* **71,** 171–180.

Willson, T. C., Paul, E. A., and Harwood, R. R. (2001). Biologically active soil organic matter fractions in sustainable cropping systems. *Appl. Soil Ecol.* **16,** 63–76.

Wilson, M. L., Rosen, C. J., and Moncrief, J. F. (2010). Effects of polymer-coated urea on nitrate leaching and nitrogen uptake by potato. *J. Environ. Qual.* **39,** 492–499.

Wrage, N., Velthof, G. L., van Beusichem, M. L., and Oenema, O. (2001). Role of nitrifier denitrification in the production of nitrous oxide. *Soil Biol. Biochem.* **33,** 1723–1732.

Wu, T.-Y., Ma, B., and Liang, B. (2008). Quantification of seasonal soil nitrogen mineralization for corn production in eastern Canada. *Nutr. Cycl. Agroecosyst.* **81,** 279–290.

Zebarth, B. J., and Rosen, C. J. (2007). Research perspective on nitrogen bmp development for potato. *Am. J. Potato Res.* **84,** 3–18.

Zebarth, B. J., Paul, J. W., Younie, M., and Bittman, S. (2001). Fertilizer nitrogen recommendations for silage corn in high-fertility environment based on pre-sidedress soil nitrate test. *Commun. Soil Sci. Plant Anal.* **32,** 2721–2739.

Zebarth, B. J., Leclerc, Y., Moreau, G., Gareau, R., and Milburn, P. H. (2003). Soil inorganic nitrogen content in commercial potato fields in New Brunswick. *Can. J. Soil Sci.* **83,** 425–429.

Zebarth, B. J., Leclerc, Y., Moreau, G., Sanderson, J. B., Arsenault, W. J., Botha, E., and Wang Pruski, G. (2005). Estimation of soil nitrogen supply in potato fields using a plant bioassay approach. *Can. J. Soil Sci.* **85,** 377–386.

Zebarth, B. J., Rochette, P., and Burton, D. L. (2008). N_2O emissions from spring barley production as influenced by fertilizer nitrogen rate. *Can. J. Soil Sci.* **88,** 197–205.

Zebarth, B. J., Dury, C. F., Tremlay, N., and Cambouris, A. N. (2009). Opportunities for improved fertilizer nitrogen management in production of arable crops in eastern Canada: A review. *Can. J. Soil Sci.* **89,** 113–132.

Ziadi, N., Simard, R. R., Allard, G., and Lafond, J. (1999). Field evaluation of anion exchange membranes as a N soil testing method for grasslands. *Can. J. Soil Sci.* **79,** 281–294.

Ziadi, N., Simard, R. R., Allard, G., and Parent, G. (2000). Yield responses of grasses to N fertilizer as related to spring soil nitrate sorbed on anionic exchange membranes. *Can. J. Soil Sci.* **80,** 203–212.

Ziadi, N., Cambouris, A. N., and Nolin, M. C. (2006). Anionic exchange membranes as a soil test for nitrogen availability. *Commun. Soil Sci. Plant Anal.* **37,** 2411–2422.

Ziadi, N., Grant, C., Samson, N., Nyiraneza, J., Bélanger, G., and Parent, L. E. (2011). Efficiency of controlled release nitrogen in potato production in eastern Canada. *Agron. J.* **103,** 1–7.

CHAPTER THREE

Biochar Application to Soil: Agronomic and Environmental Benefits and Unintended Consequences

R. S. Kookana,* A. K. Sarmah,[†,1] L. Van Zwieten,[‡] E. Krull,* *and* B. Singh[§]

Contents

* CSIRO Land and Water, Sustainable Agriculture Research Flagship, Glen Osmond, South Australia, Australia
† Soils and Landscape Responses Team, Landcare Research Manaaki Whenua, Hamilton, New Zealand
‡ Department of Primary Industries, Wollongbar, New South Wales, Australia
§ Faculty of Agriculture, Food and Natural Resources, The University of Sydney, Sydney, New South Wales, Australia
1 Current address: Faculty of Engineering, University of Auckland, New Zealand

Advances in Agronomy, Volume 112
ISSN 0065-2113, DOI: 10.1016/B978-0-12-385538-1.00003-2

Abstract

Biochar is increasingly being recognized by scientists and policy makers for its potential role in carbon sequestration, reducing greenhouse gas emissions, renewable energy, waste mitigation, and as a soil amendment. The published reviews on biochar application to soil have so far focused mainly on the agronomic benefits, and have paid little attention to the potential unintended effects. The purpose of this chapter is to provide a balanced perspective on the agronomic and environmental impacts of biochar amendment to soil. The chapter highlights the physical and chemical characteristics of biochar, which can impact on the sorption, hence efficacy and biodegradation, of pesticides. As a consequence, weed control in biochar-amended soils may prove more difficult as preemergent herbicides may be less effective. Since biochars are often prepared from a variety of feedstocks (including waste materials), the potential introduction of contaminants needs to be considered before land application. Metal contaminants, in particular, have been shown to impact on plant growth, and soil microbial and faunal communities. Biochar has also been shown to influence a range of soil chemical properties, and rapid changes to nutrient availability, pH, and electrical conductivity need to be carefully considered to avoid unintended consequences for productivity. This chapter highlights some key areas of research which need to be completed to ensure a safe and sustainable use of biochar. In particular, understanding characteristics of biochars to avoid ecotoxicological impacts, understanding the effects of biochar on nutrient and contaminant behavior and transport, the effects of aging and the influence of feedstock and pyrolysis conditions on key properties are some of the areas that require attention.

1. Introduction

The carbon-rich byproduct that is produced when biomass (e.g., agricultural crop residues, wood, waste, etc.) is heated through the process of pyrolysis in an oxygen-depleted environment is commonly referred to as biochar. However, biochar is a fairly loose term without any clear definition at the moment. According to Lehmann *et al.* (2006), the term "biochar" is a relatively recent development and evolved in conjunction with issues such

as soil management and carbon sequestration. Therefore, biochar is a term normally associated with plant biomass- or biowaste-derived materials contained within the black carbon (BC) continuum (Schmidt and Noack, 2000). This definition can include chars and charcoal, but excludes fossil fuel products or geogenic carbon (Lehmann *et al.*, 2006). Biochar differs from charcoal in regard to its purpose of use, which is not for fuel, but for atmospheric carbon capture and storage, and application to soil. Recently, the European Commission (Verheijen *et al.*, 2010) has defined biochar as charcoal (biomass that has been pyrolyzed in a zero or low oxygen environment) for which, owing to its inherent properties, scientific consensus exists that application to soil at a specific site is expected to sustainably sequester carbon and concurrently improve soil functions (under current and future management), while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health.

Two types of pyrolysis systems are predominantly used in biochar production: fast and slow pyrolysis, where the distinction relates to the heating rate and heating duration. For biochar production, slow pyrolysis is currently seen as the preferred technology as it maximizes biochar yield over production of bioenergy (Lehmann and Joseph, 2009; Sohi *et al.*, 2010). Many forms of organic material can be utilized to produce biochar, including crop- and forestry-waste products, urban-yard wastes, industrial biomass by-products, animal manures (i.e., poultry litter, dairy manure), and municipal sewage sludge.

The use of biochar as a soil additive has been proposed to simultaneously mitigate anthropogenic climate change while improving soil fertility and enhancing crop production (e.g., Glaser *et al.*, 2002, 2009; Lehmann *et al.*, 2006; Ogawa *et al.*, 2006). Indeed, adding charcoal to soil to enhance soil fertility is an age-old practice in many cultures, perhaps best exemplified by *Terra Preta de Indio* soils discovered in Amazonia, associated with native American settlements. These can be kilometer-sized fertile patches of black soils, containing charcoal, among less intensely colored and relatively infertile Oxisols (Glaser *et al.*, 2001; Lehmann *et al.*, 2003). However, the true potential of this practice in terms of both agronomic and environmental benefits has only been highlighted recently (e.g., Glaser *et al.*, 2009; Lehmann and Joseph, 2009; Lehmann *et al.*, 2006; Sohi *et al.*, 2010). Biochar application to the nutrient-poor soils is increasingly being recognized as an attractive option, given the potential agronomical and environmental benefits.

A number of reviews and studies have highlighted the potential benefits of utilizing biochar as a soil amendment. These have covered issues such as mitigation of global warming through application of stable C into soil, waste management, production of bioenergy, soil health, and productivity benefits (Atkinson *et al.*, 2010; Laird, 2008; Lehmann, 2007a,b; Lehmann *et al.*, 2006; Mathews, 2008; Ogawa *et al.*, 2006; Sohi *et al.*, 2010; Woolf *et al.*,

2010). Consequently, biochar as a soil amendment is also increasingly attracting the attention of policy makers in the United States, Australia, Europe, Japan, and some developing countries (e.g., Bracmort, 2009). The recent modeling and analysis by Woolf *et al.* (2010) demonstrate that sustainable biochar production and its soil application have the potential to make a substantial contribution to mitigating climate change. The use and functions of biochar in soils have been recently reviewed by Sohi *et al.* (2010) and potential mechanisms of achieving agricultural benefits by biochar-soil application by Atkinson *et al.* (2010). However, the hazards, risks, and other implications associated with biochar technology are yet to be fully understood (Downie *et al.*, 2011; Kookana, 2010).

The main motivation for this chapter was to provide a balanced perspective on the agronomic and environmental impacts of biochar amendments to soil. The primary objective of the chapter is, therefore, to highlight some of the agronomic and environmental issues that need to be adequately addressed for this practice to be scientifically sound and sustainable. We have placed emphasis on (i) the properties of biochars in the context of production technology and raw material used; (ii) how these properties influence key physical, chemical, and biological processes in soil; and (iii) the potential agronomic and environmental implications (Fig. 1) that may

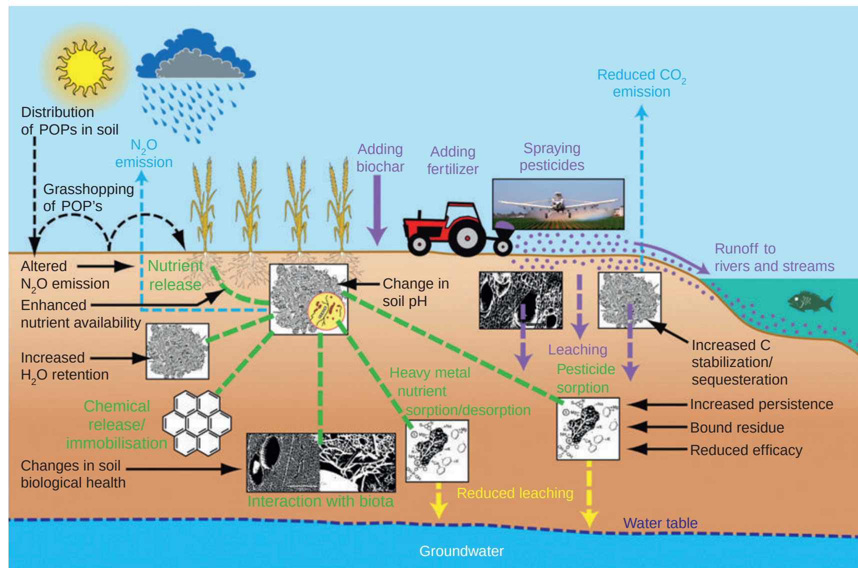


Figure 1 A schematic diagram representing a range of processes that biochar may influence in soil and the resultant agronomic and environmental advantages or disadvantages. POP stands for persistent organic pollutants (e.g., dioxins).

arise due to biochars' unique properties, composition, and production conditions. In this context, the priority areas of future research have also been identified.

2. Properties of Biochar as Affected by Feedstock and Production Technology

Feedstock and pyrolysis conditions are the most important factors controlling the physical and chemical properties of the resulting biochar. Structural characteristics of freshly made biochars, as influenced by feedstock and processing conditions, have been discussed in detail by Downie *et al.* (2009). First, the chemical and structural composition of the biomass feedstock influences the composition of the resulting biochar and, consequently, its behavior, function, and fate in soils. For instance, when wood-based feedstocks are pyrolyzed, coarse and resistant biochars are generated with high carbon contents (up to 80%), as the rigid ligninolytic nature of the source material is retained in the biochar residue (Winsley, 2007). Second, the extent of the physical and chemical alterations undergone by the biomass during pyrolysis (e.g., attrition, cracking, microstructural rearrangements) is dependent on the pyrolysis conditions (mainly temperature and residence times).

2.1. Nutrient ratios in biochar

Combustion of biomass and conversion to biochar is associated with various changes in the original nutrient content, form of nutrients, and resultant chemical structure. Maximum heating temperature and heating rate have a strong influence on the retention of nutrients as does the original composition of the feedstock. With regard to the former, the different volatilization temperatures of the different elements play a particular role on the relevant C/N/P ratios: while C begins to change and certain compounds volatilize at 100 °C, the range of oxidization and transformation products from the original C is stable over a wide temperature scale and are mainly associated with decreases in OH and CH_3 and increases in aryl C (Baldock and Smernik, 2002; Krull *et al.*, 2009). Most N and S compounds, however, volatilize above 200 and 375 °C, respectively, while K and P volatilize between 700 and 800 °C (DeLuca *et al.*, 2009). Most biochars are produced in the temperature range 450–550 °C and, as a result, tend to be relatively depleted in N and S. However, those produced from N-rich feedstocks (e.g., biosolid biochar) at the lower end of the temperature range (e.g., 450 °C) may retain up to 50% of its original N content and all of its S and, as

a result, are comparably richer in these elements than wood-based biochars produced at higher temperature (Bridle and Pritchard, 2004).

Most wood- and nut-based biochars have extremely high C/P and C/N ratios. Conversely, manure-, crop-, and food-waste biochars have much lower ratios with manure-derived biochars being the most nutrient-rich relative to C, especially in P relative to N. Nutrient-rich and ash-rich biochars lack the stability that is associated with C-rich and highly aromatic and condensed wood-derived biochars (e.g., Singh *et al.*, 2010b). Production temperature can also alter the extractability of certain nutrients and the physical and chemical properties of biochars: high-temperature biochars (800 °C) tend to have a higher pH, electrical conductivity (EC), and extractable NO_3^-, while low-temperature biochars (350 °C) have greater amounts of extractable P, NH_4^+, and phenols (DeLuca *et al.*, 2009). Mg, Ca, and Mn require even higher temperatures (above 1000 °C) and specifically the relatively high abundance of these alkaline metals (K, Mg, and Ca) can explain the increase in pH of many biochars. High concentrations of calcium carbonate ($CaCO_3$) can be found in pulp and paper sludge (Van Zwieten *et al.*, 2010a) and are retained in the ash fraction of some biochars.

2.2. Elemental ratios and aromaticity of biochar

H/C and O/C ratios in so-called van Krevelen diagrams (Killops and Killops, 2005) have been used for geologic organic matter (coal, lignite) to assess its maturity, which is a function of time and conditions of burial (temperature and depth/pressure). Applied to biochars, these provide an indication of their degree of aromaticity (the degree to which aromatic rings are connected in two- and three dimensions), which is believed to be a function of temperature. Figure 2 summarizes H/C and O/C ratios from various feedstocks and common ranges found in coal, BC, natural char, lignite, protein, carbohydrates, and lipids. However, biochar when applied to soil undergoes physical and biological oxidation, fragmentation, and carboxylation, despite its stability relative to other forms of C.

The H/C and O/C ratios decrease with increasing temperature, and it is assumed that the lower the ratio the greater the degree of aromaticity and stability. This is confirmed by NMR data suggesting that increasing temperature enhances degree of aromaticity (Baldock and Smernik, 2002; Smernik *et al.*, 2006). However, the changes are also a function of heating time. Almendros *et al.* (1990) heated a peat sample between 60 and 180 s while keeping the temperature constant at 35 °C and found that H/C and O/C ratios significantly decreased. The data also show that there is a comparably larger variability in biochars generated at temperatures below 400 °C, whereas H/C and O/C values converge above 450 °C. Recent developments in this area show that NMR is relatively insensitive to

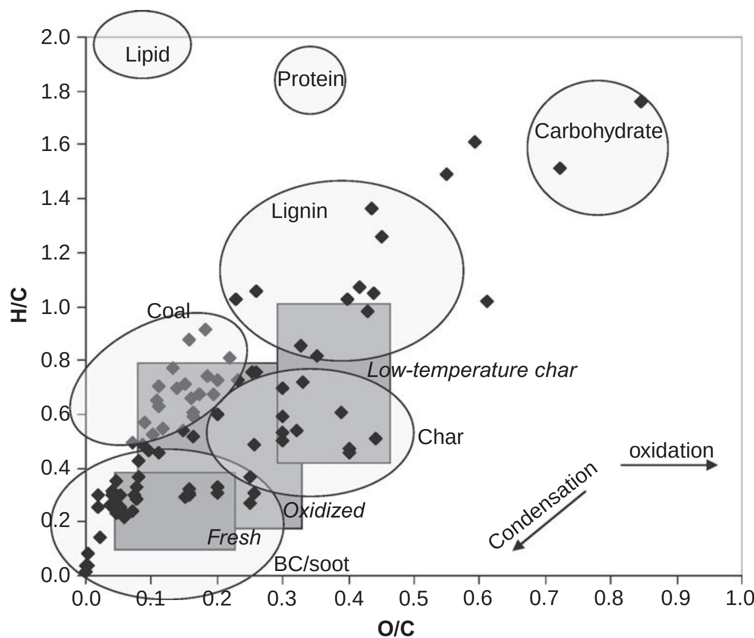


Figure 2 A range of biochar products with varying H/C and O/C ratios. Overlain as circles are typical ratios for BC/soot, char, coal, lignin, carbohydrate, protein, and lipids (from Preston and Schmidt, 2006), showing the continuum of biochar products ranging from more lignin-rich to a coal- or soot-like substance. H/C and O/C ratios of biochars can also change over time within the soil environment as indicated by the squares and chemical state in italics (after Hammes and Schmidt, 2009) showing the ranges between fresh, oxidized, and low-temperature biochar.

changes above 400 °C. McBeath and Smernik (2009) analyzed 17 heat-treated materials and confirmed that aromatic condensation increases with increasing heat-treatment temperature and that activated chars contained the most highly condensed aromatic structures. This study also highlighted the importance of starting material and heat-treatment time on aromatic condensation.

2.3. Specific surface area and microporosity of biochars

One of the unique properties of the biochars is their high specific surface area (SSA). While this key property governs most soil–biochar interactions, SSA itself is affected by the nature of the starting organic material (biomass) and the conditions under which the biochar is produced (see review by Downie *et al.*, 2009). Both SSA and microporosity of biochars have been shown to increase with temperature, as these properties are interlinked.

Nevertheless, different biochars produced from the same feedstock or biomass have very different SSA and microporosities, depending on the production technology employed (Downie *et al.*, 2009). Chun *et al.* (2004) studied a series of biochar samples produced by pyrolyzing a wheat residue (*Triticum aestivum* L.) for 6 h at temperatures between 300 and 700 °C. They observed the biochar SSA increased with increasing charring temperatures (300–600 °C); however, the SSA value of char produced at 700 °C was lower than that of char produced at 600 °C (Fig. 3). The authors speculated this to be due to microporous structures which were destroyed at 700 °C. Similarly, Brown *et al.* (2006) found that regardless of differences in the ramp rate, maximum SSA was realized at a final temperature of 750 °C (Fig. 3). The chars produced at the lowest final temperature (i.e., 450 °C) had a SSA of < 10 m^2/g, while those produced at intermediate temperatures of 600–750 °C had SSA of ~400 m^2/g. They suggested that this is most likely due to the effect of ramp rate on pore structure (Brown *et al.*, 2006).

Micropores (< 2 nm diameter, IUPAC) make a significant contribution to the increase in surface area of biochars with increasing temperatures. Yu *et al.* (2006) and Bornemann *et al.* (2007) compared biochars produced at different temperatures (at 250, 450, and 850 °C) from air-dried plant materials from *Phalaris* grass (*Phalaris tuberosa*) and red gum-wood (*Eucalyptus camadulensis*). They noted that SSA markedly increased with production temperature (from 8 to 600 m^2/g—for the wood char) and at any comparable temperature, the SSA of the wood biochar was up to two times greater

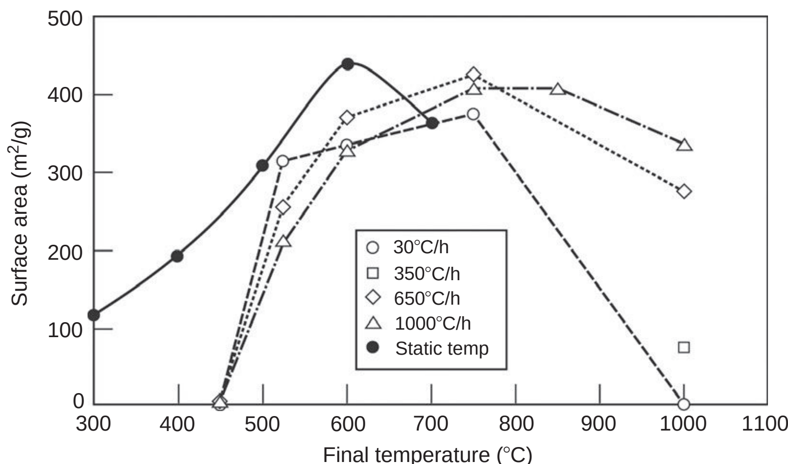


Figure 3 The specific surface areas of various biochars produced at different temperature and using different ramp rates. The legends show the ramp rates ranging from 30 to 1000 °C/h. Source: Brown *et al.*, 2006; the solid line is based on the data by Chun *et al.*, 2004, using static temperature for 1 h.

than that of the grass biochar. In terms of microporosity, the wood biochar produced at 450 °C had a very low level of microporosity and the peak maximum of pore size distribution was noted at a pore width of 1.1 nm, indicating the beginning of micropore formation at 450 °C. However, increasing temperature to 850 °C promoted the formation of micropores with peak maximum occurring at 0.49 nm. At this temperature, essentially all pores were <1 nm in pore width. Downie *et al.* (2009) observed that while elevated temperatures provide the activation energies for reaction leading to restructuring and ordering of the material, the duration of the temperature allows the extent of completion of these reactions. They noted a strong and almost linear relationship between the SSA of biochars (up to 2000 m^2/g) and the micropore volume (0.6 m^3/g). Both SSA and micropores play an important role in sequestration of chemicals by altering their bioavailability and ecotoxicological impacts on soil organisms (discussed later).

2.4. Cation exchange capacity and charge characteristics

Biochars can potentially increase the cation exchange capacity (CEC) of soils especially for highly weathered, nutrient-poor sandy soils; however, this is dependent on biochar properties and aging of applied biochar in the soil. The lack of standardized methodology of assessment of CEC in biochars makes it difficult to compare materials from different feedstocks and temperatures of production. In some cases, increasing pyrolysis temperature has been shown to decrease CEC of the biochar (Gaskin *et al.*, 2008), while in other cases, CEC increases with increasing temperature (Singh *et al.*, 2010b). The lower temperature biochar described by Gaskin *et al.* (2008) was shown to have a higher degree of oxygen surface functional groups, resulting in increased CEC. The published data suggest that biochars from woody materials tend to provide low CEC values, while non-woody plant materials such as sugarcane trash (leaf) or tree bark tend to have higher CEC values (Chan *et al.*, 2007; Gaskin *et al.*, 2008; Gundale and DeLuca, 2006; Major *et al.*, 2009; Singh *et al.*, 2010b; Van Zwieten *et al.*, 2010b; Yamamoto *et al.*, 2006).

Biochar consists of highly aromatic chemically stable components (Schmidt and Noack, 2000), and the development of negative charge from biochar oxidation in soil has been proposed in several studies (e.g., Cheng *et al.*, 2006, 2008; Hamer *et al.*, 2004; Liang *et al.*, 2006). In the Brazilian Amazon, CEC values were found to be up to two times higher in soils with biomass BC than in the adjacent soils (Liang *et al.*, 2006). The stability and oxidation of biochar in soils are affected by aging and soil environmental conditions. Cheng *et al.* (2006) observed that abiotic processes were more important than the biotic processes for the oxidation of biochar. They reported a more than six-time increase in the potential CEC

of a BC-amended soil after incubation for 4 months at 70 °C. In an another study, Cheng *et al.* (2008) observed that historical BC samples collected from a number of sites in Canada and the United States have oxidized substantially after 130 years in soils. The major changes in the historical BC as compared to the new BC included: (i) decreased C content and increased O and H contents, (ii) the formation of carboxylic and phenolic functional groups, and (iii) decreased surface positive charge and increased surface negative charge. The point of zero charge for the aged BC samples was significantly lower than the fresh BC; and unlike new biochar (New-BC_{HW}) that contribute anion exchange capacity, aged biochars (BC30 and BC7) and historical biochar exhibit significant CEC at pH $\geq$ 3 (Fig. 4; Cheng *et al.*, 2008). Biochar stability in soil is also affected by moisture status; in a 1-year incubation study at 30 °C corn biochar mineralized significantly faster under unsaturated conditions, while oak wood biochar lost most carbon under alternate unsaturated and saturated conditions (Nguyen and Lehmann, 2009).

There is limited research on the nature of functional groups on biochars; however, research on porous and activated carbon shows that acidic and basic surface sites coexist on carbon surfaces (Barton *et al.*, 1997; Biniak *et al.*, 1997; Boehm, 2002). The nature and proportion of surface functional groups on porous carbon can be modified by suitable thermal and chemical treatments.

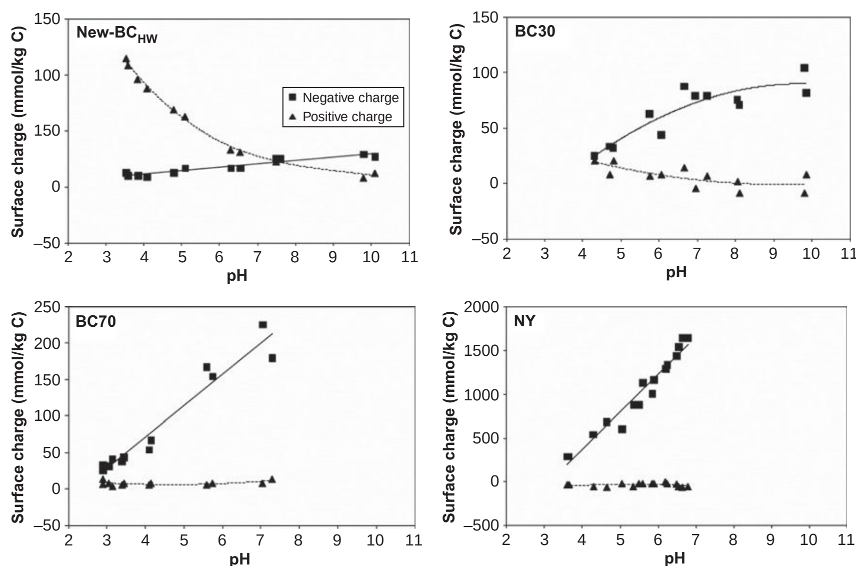


Figure 4 Cation and anion exchange capacities of a new biochar (New-BC_{HW}), aged biochars (BC30 and BC70), and a historical biochar (NY) as a function of pH (redrawn from Cheng *et al.*, 2008).

For example, gas phase oxidation of carbon increased hydroxyl and carbonyl surface groups, whereas liquid phase oxidation increased carboxylic groups (Figueiredo *et al.*, 1999), and treatment with ammonia has been used to introduce nitrogen functional groups such as pyrrole, pyridone, and pyridine (Jia *et al.*, 2002). Among the basic functional groups, pyrones are considered to be the most important (Montes-Morán *et al.*, 2004). Biochars produced at lower temperatures showed higher total surface acidity and lower basicity than the high-temperature biochars (Singh *et al.*, 2010b). The proportion of acidic functional groups on biochars, especially carboxylic groups, increased with aging (Cheng *et al.*, 2006; Nguyen and Lehmann, 2009), and this has important consequences for the sorption behavior of organic and inorganic compounds that are discussed in the later sections.

Clearly, biochars are highly carbonaceous materials with unique properties such as high SSA, micropore volume, and charge characteristics. However, feedstock and pyrolysis conditions are the most important factors controlling their physical and chemical properties. Therefore, biochars are expected to be highly heterogeneous materials with a diverse range of properties. The physicochemical properties are crucial not only in governing their biogeochemical interactions in soil environment but also in determining their agronomic and environmental impacts. These properties also contribute to the extraordinary ability of biochars to adsorb agrochemicals in soils, as discussed in some detail in the next section. Therefore, it is essential to have clear guidelines for biochar production with an understanding of feedstocks and pyrolysis parameters (Kwapinski *et al.*, 2010).

3. Biochar as an Effective Sorbent of Agrochemicals

The ability of biochars to sorb agrochemicals and contaminants is a key process that has direct bearing on not only the agronomic effectiveness of agrochemicals (e.g., herbicides, insecticides, and nutrients) but also the environmental fate and ecotoxicological impacts of contaminants. Usually, the sorption process is first to occur, as soon as the contact between sorbate and sorbent is made and in turn affects other processes ranging from chemical release, transport, bioavailability, uptake, and ecotoxicological impacts.

3.1. Sorption–desorption of pesticides and other organic compounds

Given the similarities in some of the properties of BC (including char, charcoals, and biochars) and their similar effects on the fate processes of agrochemicals or contaminants, the existing body of the literature on BC is

highly relevant and can help better understand the likely environmental and agronomic consequences of biochar amendments on soil. BC and biochars have been reported to be very effective in sorption of many natural and anthropogenic organic compounds (i.e., Accardi-dey and Gschwend, 2003; Allen-King *et al.*, 2002; Cao *et al.*, 2009; Lohmann *et al.*, 2005; Sarmah *et al.*, 2010; Yu *et al.*, 2006). For example, chars/ashes produced from burning of wheat and rice residues were reported to be up to 2500 times more effective than soil in sorbing the herbicide diuron (Yang and Sheng, 2003). A number of studies have been published in recent years demonstrating similar observations on a range of herbicides and insecticides and are listed in Table 1. Such extraordinary sorption ability of biochars arises from their high SSA, aromaticity, and microporosity. This is also consistent with the well-known relationships of chemistry of soil organic carbon (SOC) in relation to sorption of chemicals.

SOC consists of a heterogeneous mix of organic materials often classified as an amorphous, gel-like "soft or rubbery" matrix or domain and a condensed, "hard or glassy" matrix or domain (Chiou *et al.*, 1983; Weber *et al.*, 1992). These two domains have very different sorption efficiencies, and thus the amount and relative proportion of these materials in SOC influence the capacity of soil to sorb or sequester organic compounds. The extent of sorption of pesticides in soils has been found to increase with the aromaticity of SOC (Abelmann *et al.*, 2005; Ahmad *et al.*, 2001). Ahmad *et al.* (2001) noted that among various molecular components of the SOC, lignin and charcoal contents were highly correlated with the K_{oc} (sorption coefficient normalized to SOC) values of pesticides. Therefore, it is not surprising that biochars, being often highly aromatic in nature, are very effective in sorption of herbicides (Table 1). However, biochars vary widely in terms of their aromaticity.

The concentration dependency of sorption has also been found to be markedly affected by the degree of aromaticity of biochars. Sorption isotherms on highly carbonaceous sorbents including biochars have been found to be highly nonlinear (Accardi-dey and Gschwend, 2003; Chun *et al.*, 2004; Kleineidam *et al.*, 1999; Yu *et al.*, 2006). Kleineidam *et al.* (1999) investigated sorption of phenanthrene in geogenic sorbents derived from sedimentary rocks containing organic materials of different origin and maturity, including those from marine and terrestrial plant debris, lignite, coal, and charcoal and found that the K_{oc} values for these materials varied by several orders of magnitude (Fig. 5). Exceptional high K_{oc} values were noticed for charcoal and coal, and the sorption isotherms for these materials were highly nonlinear.

Not only sorption but the desorption or the release behavior of organic compounds is also strongly affected by the presence of charcoal or biochars in soil and sediments (Bucheli and Gustafsson, 2003; Jonker *et al.*, 2005; Van Noort *et al.*, 2003; Yu *et al.*, 2006). Desorption is important because the

Table 1 Selected reports on sorption, bioavailability, and degradation of pesticides in soils amended with ashes and biochars

Feedstock	Sorbent and its production temperature	Sorbate	Sorption/desorption observations	Bioavailability, persistence, and other impacts	Source
Wheat (*Triticum aestivum* L.) and rice (*Oryza sativa*) residue[a]	Ash, temperature unknown, open air burning	Ametryn and diuron herbicide	Showed up to 2500 times higher sorption than soil; >70% increase in sorption in soil (1%, wt of biochar)	Immobilization of diuron led to decreased herbicidal efficacy to barnyard grass	Yang and Sheng (2003), Sheng *et al.* (2005), Yang *et al.* (2006)
Wheat (*T. aestivum* L.)[a]	Ash, temperature unknown, open air burning	Benzonitrile herbicide	The ash was ∼2000 times more effective per unit mass than soils in sorption of benzonitrile. Amendment with 1% ash caused 10-fold increase in sorption by soil Degradation was substantially reduced in the presence of the ash	Biodegradation of benzonitrile was initially stimulated by the ash nutrients, followed by adsorptive inhibition in the presence of the ash	Zhang *et al.* (2004, 2005)
Eucalyptus spp.	450 and 850 °C	Diuron herbicide; chlorpyrifos and carbofuran insecticides	Sorption and desorption hysteresis of diuron increased with increasing biochar temperature and content in soils (to 1%)	Degradation and plant uptake of insecticides residues decreased with increased biochar content	Yu *et al.* (2006, 2009)
Dairy manure	200 and 350 °C	Atrazine	Partitioning of atrazine is positively related to biochar carbon content at 200 °C	A decrease in the aliphatic phase at 350 °C caused a reduction in atrazine sorption despite high carbon content	Cao *et al.* (2009)

(*Continued*)

Table 1 (*Continued*)

Feedstock	Sorbent and its production temperature	Sorbate	Sorption/desorption observations	Bioavailability, persistence, and other impacts	Source
Wheat (*Triticum aestivum* L.)[a]	Ash, temperature unknown, open air burning	Atrazine	Sorption on char alone was 800–3800 times greater than sorbed by the soils. Successive desorption experiments showed that char-amended soils contained higher nondesorbable fractions of atrazine than soils without char amendment	The presence of char reduced mineralization of atrazine by *Pseudomonas* sp. strain. ADP and $^{14}CO_2$ production decreased by 11% and 20% in the char-amended soils and char, respectively	Loganathan *et al.* (2009)
Mixed sawdust	500 °C, fast pyrolysis process	Atrazine and acetochlor	Low surface area of char noted possibly due to bio-oil deposition. The addition of biochar (5%, w/w) to soil increased the sorption of atrazine and acetochlor compared to non-amended soils	A decrease in dissipation rates of these herbicides (by a factor of 2–3) was noted in char-amended soil (5%, w/w)	Spokas *et al.* (2009)
Greenwaste—pruning mixture of maple, elm, and oak woodchips and barks	Pyrolysis under the oxygen-limited condition for 60 min at 450 °C	Atrazine and simazine	Biochar showed high sorption affinity for the two herbicides. A competitive sorption noted between these two pesticides on the biochar. Sorption on biochar was pH-dependent	Sorption equilibrium was faster on finer fraction of biochars	Zheng *et al.* (2010)

[a] The material was produced by open air burning of wheat residue and therefore may not be a biochar but ash.

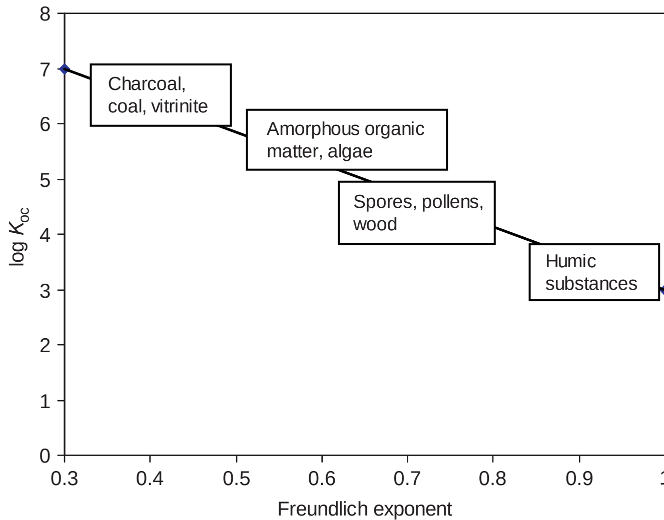


Figure 5 Variations in K_{oc} and Freundlich exponent in sorption of organic compounds on different types of carbons (after Kleineidam *et al.*, 1999).

bioaccessibility, bioavailability, efficacy, and toxicological impact are directly linked to the desorption behavior, as the compound needs to be released back into solution to be effective or have any impact on target or nontarget organisms. Studies comparing sorption and desorption isotherms for diuron herbicide and of pyrimethanil fungicide in soils amended with different biochars have reported relatively flat desorption isotherms (Yu *et al.*, 2006, 2010) indicating an apparent sorption–desorption hysteresis (Fig. 6). Specific adsorption, entrapment into micropores and partitioning into condensed structures of soil organic matter are often the causes for sequestration of chemicals (e.g., Huang *et al.*, 2003; Weber *et al.*, 1992). However, our understanding on the various microscale processes controlling sorption–desorption of organic compounds to biochar particles in soils and sediments is limited.

Not all biochars are expected to have similar sorption–desorption behaviors. However, in most published sorption studies, biochars were produced from either one fixed biomass or only a small range of temperatures. A study by James *et al.* (2005), however, employed a range of different pyrolysis temperatures for three species of softwood to test sorption of phenanthrene. They concluded that in addition to surface area, heterogeneous surface properties contribute to sorptive ability of biochars. Spokas *et al.* (2009), working with a biochar produced from sawdust at 500 °C, noted that, on a mass basis, their biochar was an even less effective organic sorbent for two herbicides than other forms of SOC. Due to limited

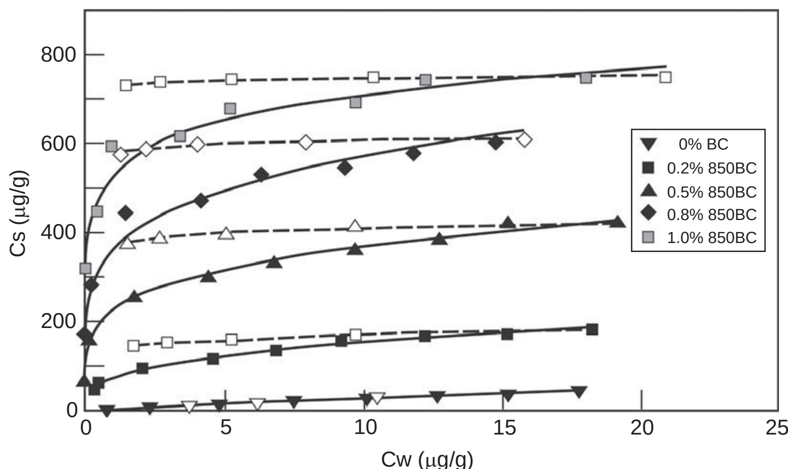


Figure 6 Sorption–desorption isotherms of diuron herbicide showing an increased sorption (and its nonlinearity) and sorption–desorption hysteresis with increase in biochar content of a soil (BC 850 is black carbon produced at 850 °C). Cs represents concentration (mg/kg) on solid phase, and Cw is the solution concentration (mg/L) at sorption equilibrium (redrawn from Yu *et al.*, 2006).

published work so far, the sorption heterogeneity of biochars and their potential implications remain largely unexplored.

3.2. Retention and release of nutrients and heavy metals

It is well known that activated carbon-based products are strong adsorbents of micronutrients and toxic metals (Budinova *et al.*, 1994; Huang, 1978). However, there is limited research on adsorption of metals on biochars. Some recent studies indicate that biochars have significant potential for metal adsorption that varies with the properties of both biochars and metals. Mohan *et al.* (2007) studied the adsorption of As, Cd, and Pb on chars produced by fast pyrolysis at 400 and 450 °C from oak bark, pine bark, oak wood, pine wood, and a commercial activated charcoal. The observed maximum adsorption of As was noted in 3–4 pH range and that of Pb and Cd in 4–5 pH range. Among the chars, oak bark char adsorbed maximum Pb, Cd, and As which was attributed partly to the higher SSA and pore volume of the char. The authors considered caion exchange as the main mechanism for the metal adsorption. Adsorption of Cd, Cu, Ni, and Pb was investigated by Uchimiya *et al.* (2010b) from a mixture containing these metals by chars produced by pyrolysis of broiler litter manure at 350 and 700 °C and their steam-activated analogues. All the chars adsorbed metals in the sequence Ni < Cd < Cu < Pb. Significant decrease in solution pH was observed with heavy metal immobilization that was partly contributed

to the exchange of protons by divalent cations. However, the total metal adsorption was 3–4 order of magnitude greater than the amount of proton released and other mechanisms: (i) complexation of metals by surface groups (e.g., –O–, =O, and –CHO) that do not release protons, (ii) exchange with alkali and alkaline cations, and (iii) precipitation of metal hydroxides (Uchimiya *et al.*, 2010b).

Namgay *et al.* (2010) investigated the biochar sorption of As, Cd, Cu, Pb, and Zn and plant availability and uptake of these trace elements from a sandy soil amended with wood biochar produced at 550 °C (Fig. 7). The sorption sequence of the metal(loid)s on the biochar for initial loadings up to 200 μM was Pb > Cu > Cd > Zn > As, which is similar with the sorption behavior of these elements on soil organic matter and activated carbon. The decrease in equilibrium solution pH with increasing sorption of metallic cations was suggested due to the exchange of metallic cations with protons; arsenate sorption increased the solution pH that possibly was caused by arsenate exchange with OH^- from biochar surfaces. Biochar application to soil decreased the concentration of As, Cd, and Cu in maize shoots from soil which were spiked with 50 mg/kg of these elements; this was attributed to the sorption of the metal(loid)s by biochar. The effects of biochar on Pb and Zn availability to plants were inconsistent. The results

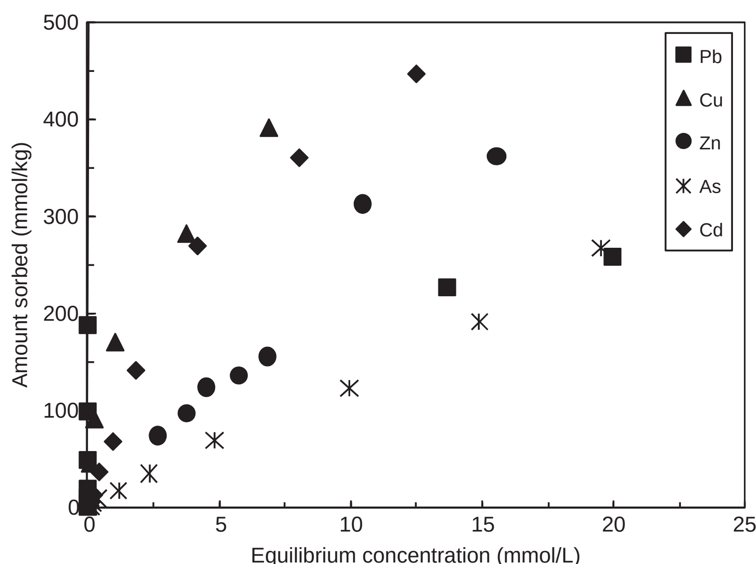


Figure 7 Sorption isotherms of As, Cd, Cu, Pb, and Zn onto a wood biochar, initial solution concentration of the elements 2–800 μmol, initial solution pH 7 and 0.01 M $Ca(NO_3)_2$ background electrolyte. Source: Namgay *et al.*, 2010, reproduced with permission from CSIRO Publishing, Melbourne, Australia.

from the research cited above highlight the need for a thorough understanding of the effects of biochar on the bioavailability of metal(loid)s in agricultural or contaminated soils. The characteristics of biochar and their interaction in soils need to be understood to determine possible interactions with metal contaminants.

3.2.1. Effect of "aging" of biochars on sorption

Due to the propensity of biochars to undergo a range of biogeochemical interactions in soil, their properties are expected to change with time in soil, a process commonly referred to as "aging." Sorption of environmental constituents, especially natural organic matter (NOM) and oxidation reactions are major contributors in aging of biochars (Uchimiya *et al.*, 2010a). It has been shown that NOM can suppress sorption of organic contaminants on environmental BC by blocking micropores (Pignatello *et al.*, 2006). The presence of various metallic ions such as copper and silver at environmental relevant concentrations (50 mg/L) may also alter surface chemistry and/or pore-network structure of the char through complexation (Chen *et al.*, 1997).

In terms of mineral–biochar interactions, it is possible that with time mineral surfaces may cover the reactive surfaces of biochar and thereby mask the true sorption capacity of biochars for organic compounds such as pesticides and other agrochemicals. The studies based on sorption of pesticides before and after removal of paramagnetic materials (e.g., sesquioxides) from carbon surfaces by hydrofluoric acid treatment (needed for NMR studies) have shown that sorption on natural charcoal in soils increases by a factor of 2–3 after such a treatment (e.g., Ahangar *et al.*, 2008; Singh and Kookana, 2009). This has been attributed to the organomineral interactions gradually masking sorptive surfaces of aged charcoal in soils.

As highlighted earlier, high specific surface areas, microporosity, and charge characteristics make biochars very efficient sorbents for a range of organic chemicals which are of agronomic and environmental importance. However, such behavior may change with time in soils due to myriad of biogeochemical interactions biochar is likely to undergo in soils. In the following sections, we discuss how biochar–chemical interactions may result in beneficial as well as unintended consequences for crop productivity, soil health, and the environment.

4. Agronomic Implications

Biochar has the potential to alter a wide range of chemical, physical, and biological properties of soil (Joseph *et al.*, 2010). Depending on the feedstock used, biochars can contain significant nutrient content (e.g., Chan and Xu, 2009; Chan *et al.*, 2008; Singh *et al.*, 2010b; Van Zwieten *et al.*,

2010a,b) and offer direct nutritional value. Some biochars can also help improve nutrient use efficiency (indirectly through nutrient sorption), particularly in soils where leaching or off-site migration of nutrients is a concern. Nutrient use efficiency is important both from the water quality and from the greenhouse gas emissions perspective (Lehmann and Joseph, 2009).

Several articles have already articulated agronomic benefits that may potentially be realized from using biochar as a soil amendment (e.g., Atkinson *et al*., 2010; Glaser *et al*., 2009; Lehmann and Joseph, 2009; Lehmann *et al*., 2006; Sohi *et al*., 2010). Figure 1 summarizes some of the potential benefits and implications associated with biochar amendments to soil, but caution is warranted as some potential negative impacts are also possible. These negative impacts can include binding and deactivation of agrochemicals (herbicides and nutrients) in soil, release of toxicants that may be present in biochar (e.g., heavy metals), oversupply of nutrients, increase in EC and pH, and impacts on germination and soil biological processes. Here, we explore some of these unintended implications that have not been fully appreciated in the biochar–soil literature so far.

4.1. Herbicide efficacy and development of weed resistance

Biochar is a particularly interesting material from the standpoint of its ability to bind agrochemicals and potentially reduce their efficacy. Indeed, the incorporation of a small amount of some fresh biochars in soil has been shown to strongly bind organic compounds (e.g., pesticides) and inhibit their microbial degradation resulting in reduced bioavailability and efficacy to plants (Yang *et al*., 2006; Yu *et al*., 2009; Zhang *et al*., 2005). Numerous examples demonstrating increased sorption or reduced bioavailability of pesticides following biochar application to soil exist in the literature (Table 1). These observations have direct implications for the effectiveness of pesticides in controlling target organisms as well as on the label rates required for pest control.

In Australia, some 35 years ago, Toth and Milham (1975) observed the effect of combustion materials produced by burning paspalum (*Paspalum dilatatum* L.) under a wide range of conditions and noted that these adsorbed appreciable quantities of diuron from aqueous solution. However, these were ash materials and not biochars. They noted that one of the two ash-C products caused a significant reduction in the phytotoxicity of ≥ 16 kg diuron/ha. They subsequently reported markedly reduced efficacy (by 60%) of two preemergent herbicides, thiobencarb (*S*-eithyl hexahydro-1,4-azepine-l-thiolcarbamate) and molinate (*S*-(4-chlorobenzyl)-*N.N*-diethylithiolcarbamate), when the herbicides were applied over rice stubble ash (Toth *et al*., 1981). Similarly, decreased phytotoxicity of diuron

herbicide was noted when applied over the ash of recently burned kangaroo grass (*Themeda australis* (R.Br.) Stapf; Toth *et al.*, 1999).

Recent studies have confirmed similar reductions in the efficacy of pesticides in the presence of biochars in soil. For example, Yang *et al.* (2006) reported reduced herbicidal efficacy of diuron, while Xu *et al.* (2008) reported reduced efficacy of clomazone to control weeds in soils amended with so-called wheat and rice straw biochars,[1] respectively. The study by Yang *et al.* (2006) highlighted that with increasing biochar content in soil, much higher rates of application of herbicides were needed to get the desired weed control. Their study showed that even doubling the application rate of diuron failed to control the weed growth in the presence of 0.5% of wheat biochar in soil (as shown in Plate 1). It was noted that even at low application rate (0.1%), biochar in soil would appreciably reduce the bioavailability of diuron. It is worth noting that Yang *et al.* (2006) used materials produced by open air burning of wheat/rice residues, and thus these may more appropriately be termed as ash materials (as per some earlier publications using these materials) rather than biochars. The biochars produced through pyrolysis of woody materials are likely to be more effective

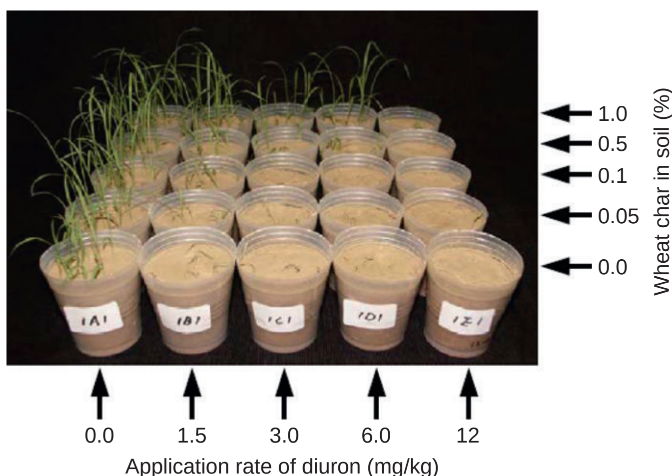


Plate 1 Weed control of Barnyard grass with diuron herbicide applied at different application rates to a soil amended with varying rates of wheat straw residue biochar. Source: Yang *et al.*, 2006, reproduced with permission from Elsevier.

[1] Please note that in these studies and in some others, the crop residues were burnt in an open field. Therefore, strictly speaking, these are not biochars but ash materials. However, since the authors used the term char or biochar in some of their publications, the term has been retained in the subsequent discussion on their work.

in reducing the herbicide efficacy due to their greater sorption affinity to herbicides than grass biochars (Bornemann *et al.*, 2007; Yu *et al.*, 2006).

It is noteworthy that the reduced efficacy of soil-applied herbicides in biochar-amended soils may result in a scenario of essentially "underdosing" (less than the required rate of application) of herbicides, unless applications are adjusted based on biochar content of soils. Such under-dosing, if persists, could lead to faster development of weed resistance. Unintended under-dosing has previously been noted to exacerbate the development of weed resistance for ryegrass (*Lolium rigidum*) in Australia (Neve and Powles, 2005; Powles *et al.*, 1996). The need for increased dose of herbicides (or insecticides) in soils amended with biochars would clearly be an increased cost burden for growers and thus could be a major disadvantage. It has been well recognized that the adoption of environmentally attractive practices such as minimum or zero till has been significantly constrained by the increased cost of chemical weed control in some areas (D'Emeden and Llewellyn, 2006). Therefore, serious considerations are warranted to this potential agronomic and economic disadvantage associated with biochar application to soil. However, biochar in soils is not expected to affect the efficacy of contact herbicides directly applied on plants. Further, whether biochars would lose or retain the capacity to inactivate herbicides with time due to organomineral and biological interactions in soil remains to be seen.

4.2. Nutrient immobilization and release

The potential benefits of biochar to improving soil fertility through nutrient addition and improvements in fertilizer-use efficiency are well recognized, as stated above. However, unintentional consequences such as nutrient sorption, increased leaching of some nutrients, and increased EC need consideration prior to biochar application to soil.

The changes in N dynamics following biochar application are not fully understood (Clough *et al.*, 2010; Lehmann, 2007a; Singh *et al.*, 2010a). However, it has been suggested that weathering of biochar in soil can lead to immobilization of N (Singh *et al.*, 2010a; Yao *et al.*, 2009). It has been noted that biochar at high application rates (10% or 20%, w/w) can effectively reduce NH_4^+ leaching in contrasting soils (Lehmann *et al.*, 2003). But this effect depends on biochar type and soil and their contact time (aging). Singh *et al.* (2010a) demonstrated that while freshly added biochars had little effect on NH_4^+ leaching, upon aging in soil (around 5 months), the wood- and poultry litter-based biochars produced at 550 °C were able to reduce leaching of NH_4^+ by 55–65% in an Alfisol. In contrast, however, no effects were observed with the biochars produced from the same feedstocks at 400 °C. The above four biochars (two feedstocks and two temperatures) significantly reduced NH_4^+ leaching in a Vertisol, a soil inherently less prone to NH_4^+ leaching due to high smectite content in the clay fraction

(Singh and Heffernan, 2002). Biochar applications may result in increased initial leaching of nutrients (e.g., nitrate) from soil, especially when the biochars have high N content (Singh *et al.*, 2010a).

As biochar alters N dynamics in soil, it can be expected to influence gaseous losses of N. Loss of N as N_2O provides a small, but environmentally significant route for N loss from soil to the atmosphere. Nitrous oxide is produced through a range of mechanisms in soil including nitrification, nitrifier denitrification, and denitrification (Baggs, 2008), and it has been suggested that biochar can play a significant role in altering these processes (Singh *et al.*, 2010a; Van Zwieten *et al.*, 2009, 2010b). Incorporation of biochar into soil has been reported to either stimulate or suppress depending on initial soil moisture content (Rondon *et al.*, 2007; Singh *et al.*, 2010a; Yanai *et al.*, 2007) or make no change in N_2O emissions (Clough *et al.*, 2010). Different biochar–soil combinations may show varying results. Further studies on biochar application on N dynamics in soils are warranted (Clough *et al.*, 2010; Lehmann, 2007a).

While the artificial aging of biochar in the presence of humic substances resulted in immobilization of N (Yao *et al.*, 2009), the availability of other nutrients, particularly P, Ca, Mg, K increased. Sinclair *et al.* (2010) noted increases in plant available P following amendment with animal manure biochar in a field studies on a ferrosol, a result not observed with greenwaste biochar. Conversely, high rates of biochar application (4.4% and 11%, w/w) to a sandy Yellow Earth resulted in a small but statistically significant reduction in plant available P (Van Zwieten *et al.*, 2010c). It has been suggested that biochar may increase the EC of leachate, attributed to loss of Na and K from the biochar–soil matrix (Lehmann *et al.*, 2003; Novak *et al.*, 2009). It is clear that impacts on nutrients are dependent upon the properties of both soil and biochar. The wide range of effects on nutrient dynamics from biochar application to soil is still poorly understood, as effects can be highly soil and biochar specific.

Given the ability of biochar to immobilize a wide range of organic and inorganic chemicals, it is conceivable that by applying biochar to soil could influence the plant uptake of a range of organic compounds or micronutrients and their unbalanced uptake may affect even the quality of the produce. This aspect has not received any attention in the literature so far.

4.3. Soil pH and Al toxicity

Biochars can have a wide range of pH values ranging from slightly acidic to alkaline (Chan and Xu, 2009). Their ability to provide a liming effect is once again dependent upon both the feedstock and processing temperature; increasing pyrolysis temperatures generally led to high pH values of biochars (Singh *et al.*, 2010b). Biochars produced from papermill wastes have liming values equivalent to up to 33% that of agricultural lime due to the presence

of calcite (Singh *et al.*, 2010b; Van Zwieten *et al.*, 2010a). The acid neutralizing capacity of biochars derived from wood or greenwaste tends to be smaller than from higher ash feedstocks such as animal manures.

Changes in soil pH can influence the bioavailability of toxic elements such as Al. Van Zwieten *et al.* (2010a) demonstrated an increase in soil pH from 4.2 to between 5.4 and 5.9 with the application of 1% (w/w) papermill biochar in a ferrosol; resulting in a concomitant reduction in exchangeable Al from ca. 2 to <0.1 cmol(+)/kg. Steiner *et al.* (2007) showed available Al decreased from 4.7 mg/kg to below detection in an Oxisol. Similar effects were observed in weathered tropical soils in Indonesia (Yamamoto *et al.*, 2006). It has been shown that Al toxicity could also decrease due to its complexation to high-molecular-weight organic compounds (Alleoni *et al.*, 2010).

4.4. Plant germination and seedling growth

Some research suggests that biochars may contain some phytotoxic compounds (Rogovska *et al.*, 2010) that can impact plant germination, or plant growth. Conversely, other attributes of biochar, such as sorptive capacity for allelochemicals (Rogovska *et al.*, 2010), may indeed result in increases in plant germination. Limited work so far has reported both stimulation and inhibition of germination, depending on soil type and pyrolysis conditions associated with the biochars tested. For example, biochars derived from papermill waste (Van Zwieten *et al.*, 2010a) when applied at 10 t/ha (~1% on weight basis) either significantly improved germination or wheat in Ferrosol, but had no significant effect on other indicator crops including radish or soybean in either Ferrosol or Calcarosol. In contrast, Kwapinski *et al.* (2010) showed that the growth of maize (*Zea mays* L.) seedlings was found to be inhibited by soil amendments with a miscanthus (*Miscanthus* × *giganteus*) biochar formed at 400 °C for 10 min, but stimulated by the one produced at 600 °C for 60 min. Keller *et al.* (2010) assessed the phytotoxic impacts of tar-enriched biochar on Black Seeded Simpson Lettuce (*Lactuca sativa*). Their biochar was derived from sorghum feedstock using fast pyrolysis without N_2 purge. The authors noted increased germination and seedling growth of the test plant even with tar-enriched biochar amendment up to 10% in soil.

4.5. Soil biological properties

Published studies so far show that most biochars constitute a medium that encourages microbial population. For example, Pietikäinen *et al.* (2000), Baldock and Smernik (2002), and Hamer *et al.* (2004) reported enhanced microbial activity when biochars were inoculated. However, the potential

toxic effects on soil microorganisms of residual bio-oils and recondensation products adsorbed on the surfaces of some biochars have also been reported in the literature (McClellan *et al.*, 2007).

Biochar surfaces may serve as favorable sites for microorganisms due to greater concentrations of adsorbed nutrients (Pietikäinen *et al.*, 2000). Their specific pore size characteristics may also exclude predators such as protozoa and nematodes and thus favoring the colonization by bacteria and fungi (Thies and Rilling, 2009; Warnock *et al.*, 2007). It is not clear whether microbes actively infiltrate biochar particles or colonize the outer surfaces containing adsorbed nutrients and fresh organic matter (Hammes and Schmidt, 2009; Lehmann and Joseph, 2009). Enhanced colonization but decreased respiratory activity of microbes has been observed in biochar-amended soils (Thies and Rilling, 2009), and Weyers *et al.* (2010) also found that soil respiration decreased with increasing application rate of biochar. Thies and Rilling (2009) noted a shift in the bacterial-to-fungal ratio as C/N ratios became wider. Increased mycorrhizal colonization has been observed when soils were amended with some biochars (Solaiman *et al.*, 2010), apparently indirectly by increasing P solubility in soils (e.g., Gundale and DeLuca, 2006; Solaiman *et al.*, 2010). In contrast, poultry litter biochars have been shown to decrease mycorrhizal colonization (Treseder, 1998).

Recently, Steinbeiss *et al.* (2009) studied the effect of hydrothermally synthesized biochars from glucose and yeast on the microbial community when added to soil. Despite not being representative of common feedstocks, the study on these biochars showed interesting differences between the two model components: yeast-derived biochar (seen to be analogous to easily degradable biochar) showed a strong stimulation of soil microorganisms and particularly fungi, but the glucose-derived biochar did not show the same effect. They noted that the addition of both biochars increased soil respiration in the first 12 weeks compared with the control. However, some other workers have reported an opposite effect of biochar addition to soil (Jin *et al.*, 2008; Liang, 2008). For example, in the study by Jin *et al.* (2008), the total respiration and the respiratory rate (measured over an 8-week period at the end of the cropping season) were found to decrease with increasing amount of a corn-derived biochar (at varying rates 0–30 t/ha) in soil.

Due to the relatively short duration of the experiments in the above studies definitive conclusions cannot be drawn. How microbial communities change over time in biochar-amended soils is not well studied yet. It is not clear if microbes could thrive on the nutrients adsorbed on to biochars (Thies and Rilling, 2009). Clearly, this is an area that deserves much greater attention in future to establish the long-term effect of biochar application in soil on soil biological health.

5. Environmental Implications

Combustion is widely recognized as a process that generally leads to formation of certain toxic compounds and therefore an obvious question arises: do biochars contain toxicants associated with their production? The question becomes even more relevant when feedstock itself may be sourced from waste materials (e.g., biosolids) containing contaminants or their precursors. In the following section, we have reviewed research on biochars either as a source of contaminants or as materials influencing environmental fate, transport, and potential ecotoxicological impacts of contaminants.

5.1. Biochar as a potential source of toxicants

Presence of combustion-driven toxic organic compounds such as polynuclear aromatic hydrocarbons (PAHs), chlorinated hydrocarbons, and dioxins is often suspected in biochar products (Chagger *et al.*, 1998). PAHs consist of fused aromatic rings and generally occur in oil, coal, and tar deposits, and are by-products of burning of fossil fuel or biomass. They are of a concern due to the carcinogenic, mutagenic, and teratogenic nature of some of these compounds. Dioxin is a general term for a large group of polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). These are part of first 12 persistent organic pollutants (POPs) covered under the Stockholm Convention (www.pops.int). However, very little is so far known about the contents of such organic toxicants in biochars. While the exact mechanisms of formation of these toxicants during combustion of biomass are unclear, these are speculated to be synthesized through a catalytic assembly of dioxin structures from C, O_2, and Cl at a temperature window of 300–325 °C and other multistep reaction processes in the post-combustion zone (Chagger *et al.*, 1998), often catalyzed by copper and iron.

Brown *et al.* (2006) analyzed different PAH congeners in a range of synthetic biochars produced from small blocks of pitch pine wood pyrolyzed using ramp rates between 30 and 1000 °C/h and with maximum temperatures between 450 and 1000 °C. A natural char was also included by gathering charred pine from a site of a prescribed burn. They found that all wood chars contained measurable quantities of PAHs and the concentrations were dependent on carbonization temperature and source (natural and synthetic). A comparison of total PAH contents (the sum of 40 different PAHs) among the chars produced at different final temperatures (but all with same ramp temperature of 650 °C/h) showed a strong dependence on the production temperature (16 mg/kg in the 450 °C char material, 7 mg/kg in the 525 °C char, and only 3 mg/kg for the 1000 °C char).

The natural char had a much higher value with a total PAH concentration of 28 mg/kg. This trend in temperature dependence was also noted for many individual PAHs. The chars produced at low-temperature contained a higher concentration of low-molecular-weight/high-vapor-pressure PAHs, whereas the high-temperature char contained higher concentrations of the higher-molecular-weight/lower-vapor-pressure PAHs. Recently, Singh *et al.* (2010b) analyzed the PAH contents of 11 biochars, made from five feedstocks: *Eucalyptus saligna* wood (at 400 and 550 °C both with and without steam activation), *E. saligna* leaves (at 400 and 550 °C with activation), paper mill sludge (at 550 °C with activation), and poultry litter and cow manure (each at 400 °C without activation and at 550 °C with activation). The PAHs concentrations in all samples were well below <0.5 mg/kg, the Australian guideline value for PAH concentration in soil (NEPM, 1999). Based on the few studies above, and considering likely dilutions in soils, the levels of PAHs in soils introduced through biochars may be acceptable. More work, however, is needed to confirm this, especially for waste-driven biochars. Moreover, since highly hydrophobic compounds (e.g., PAHs, dioxins) are strongly sorbed by biochars, the current extraction procedures may need to be modified to get a more accurate estimation of the total loads of such contaminants on biochars (even if these are not readily bioavailable).

Some biochars may be rich in metal contents and may be of concern if applied to soil without due consideration. For example, Zn contents of *E. saligna* wood and poultry litter biochars were found to range from 1312 to 1661 mg/kg, and from 1449 to 1642 mg/kg, respectively (Singh *et al.*, 2010b). Soil application of these biochars at high rates could build up soil Zn levels that could be potentially toxic to plants and soil microorganisms. It is noteworthy that the current Australian guidelines for unrestricted use of biosolids suggest a range of 200–250 mg Zn/kg on dry weight biosolids (NRMMC, 2004). Similarly, Cu content of poultry biochars has been found to be high (805–1034 mg/kg; Gaskin *et al.*, 2008); however, poultry litter biochar from Australia had a lower Cu concentration of 310 mg/kg (Van Zwieten *et al.*, 2010b). The levels of toxic metals in biochars depend on the original content of metals in the feedstocks and processing conditions, and the potential impact on soil would depend on the soil type and their ability to immobilize and detoxify the contaminants (see Section 3).

5.1.1. Contaminants in biochars from wastes

Waste management is one of the attractive elements associated with the biochars technology (Lehmann *et al.*, 2006). Therefore, the feedstock source—especially when biochars are produced from waste material (e.g., municipal solid waste—MSW, sewage sludge, or industrial waste)—may influence the nature and extent of contaminants present in the final biochar product and/or formed during the production process. MSW is a complex mixture of varying components, consisting of cellulose- or lignin-derived

material, polymer-based materials, and inorganic materials. Vassilev and Braekman-Danheux (1999) studied the trace elements in chars generated by combustion of MSW. They found that a number of trace elements (Ag, Cd, Cl, Cr, Cu, Ho, I, Pb, Pr, Re, Sb, Sm, Sn, and Zn) in these chars were present at concentrations significantly higher (> 10 times) than the respective world-wide averaged values for coals. More recently, Yoshida and Antal (2009) studied the suitability of sewage sludge as feedstock for the production of biochar. They produced biochar from a sludge with low heavy metals content using flash carbonization technique and found that the product was acceptable for land application according to U.S. EPA regulation 40 CFR Part 503. Conversely, Van Zwieten *et al.* (2010b) analyzed biochar from biosolids produced at 550 °C, and found Zn concentrations (890 mg/kg) in the biochar that exceeds the Grade B biosolids guidelines of New South Wales (Australia; NSW EPA, 1997). Other metals analyzed including As, Cu, Cd, Pb, Ni, and Se were suitable for land application (NSW EPA, 2009).

The studies cited above highlight the potential of contaminants to be present in pyrolysis products and the importance of careful choice of waste as a feedstock. The makeup of the waste used as a feedstock may contain the precursors for other toxicants that may be formed during the pyrolysis process. Currently, little is known of the potential production or transformation of contaminants (which may be present in waste material used as a feedstock) during the biochar manufacturing process.

5.2. Mobilization/immobilization of cocontaminants

Organic and inorganic contaminants coexist in soil environments, and thus the effects of coadsorbed metals on adsorption of organics have been investigated on charcoals (Cao *et al.*, 2009; Chen *et al.*, 2007). Coadsorption of Cu^{2+} decreased the sorption of both polar (2,4-dichlorobenzene) and nonpolar compounds (dichlorobenzene and naphthalene) between 30% and 60% on wood charcoal (Chen *et al.*, 2007). Chen *et al.* (2007) assumed that hydration shells of water are formed in the surface complexation of Cu^{2+} which directly competes with the organics for the adsorption sites on the charcoal. In contrast to Cu^{2+}, coadsorption of Ag^{+} increased the sorption of organics by charcoal and this effect contributed to the decreased hydrophilicity of charcoal surfaces. Similarly, little competition for sorption was noted when Pb and atrazine were coadsorbed on a dairy manure biochar (Cao *et al.*, 2009). This was due to completely different sorption processes, that is, precipitation for Pb and surface sorption for atrazine were involved in the sorption of the coadsorbents.

In order to investigate the impact of aging on the effectiveness of biochars on the immobilization of Cu^{2+}, Cd^{2+}, and Ni^{2+} and release of S, Uchimiya *et al.* (2010b) used NOM with known carboxyl contents and studied the mobilization and immobilization of these elements from a soil.

They noted that while biochar amendment generally enhanced the immobilization of heavy metal contaminants (regardless of biomass source and pyrolysis conditions), the addition of reference Suwannee River NOM or Elliott soil humic acid (having high carboxyl content) mobilized Cu^{2+} otherwise retained by soil. This was possibly due to complex formation with metal ion-coordinating organic fractions and competition with metal ions for the sorption sites. Their study suggested that organic fraction of biochars, and NOM having high carboxyl contents, may mobilize the native pool of certain heavy metals (e.g., Cu^{2+}) in soils. Competition for sorption sites and potential mobilization of cocontaminants or release of native pool of chemicals is dependent on the nature of biochars, soils, and chemicals involved.

5.3. Decreased bioavailability and increased persistence of chemicals

Generally, organic compounds become less bioavailable with time in soils or sediments (see review by Alexander, 1995; Hunter *et al.*, 2010; Semple *et al.*, 2003). In this context, the presence of highly microporous hydrophobic sorbents (such as biochars, BC) may be particularly effective in reducing their bioavailability with time. Indeed, the physicochemical characteristics of the sorbent matrix have been shown to have profound effects on the bioavailability of organic compounds (Luthy *et al.*, 1997). For example, tests with model sorbents by Nam and Alexander (1998) showed that with glass and polystyrene beads (with no porosity), phenanthrene was rapidly mineralized, whereas with porous polystyrene beads (containing 5 or 300–400 nm pores), little of the compound was desorbed and only $<7\%$ of sorbed phenanthrene was mineralized. Microporosity of biochar, therefore, is expected to influence the bioavailability of agrochemicals.

Incorporation of a small amount of biochar in a soil has been shown to inhibit the microbial degradation of pesticides and thereby to increase their persistence in the environment (Yu *et al.*, 2009; Zhang *et al.*, 2005; Table 1). For example, Yu *et al.* (2009) amended soils with different amounts of biochars produced at two different temperatures (450 and 850 °C) to a level of 0–1% by weight. Biodegradation and plant uptake of two insecticides (carbofuran and chlorpyrifos with differing hydrophobicities) by spring onions (*Allium cepa*) were studied. They noted that the bioavailability of the two pesticides to microorganisms (biodegradation) as well as for plant uptake (and efficacy by inference) decreased with increasing biochar content in soil. This resulted in prolonged persistence of the compounds in biochar-amended soils. Over 35 days, 86–88% of the pesticides dissipated from the unamended soil, whereas only 51% of carbofuran and 44% of chlorpyrifos disappeared from the soil amended with 1.0% biochar produced at 850 °C. Several recent studies have further demonstrated the

increased persistence of herbicides in soils amended with biochars (Table 1). Whether the slower degradation of pesticides in biochar-amended soils would result in buildup of residues and if such (bound) residues have any environmental relevance, is not clear.

5.4. Impact on transport of agrochemicals and contaminants (including POPs)

POPs produced and used in industrialized nations are a cause of great concern globally due to their persistent, bioaccumulative, and toxic nature as well as their propensity to travel long distances to affect even remote and uninhabited parts of the globe (Wania, 2006). The partitioning process plays a crucial role in determining their environmental fate, transport, accumulation, impact on biota, and food safety. Due to their hydrophobic nature, most POPs have a strong affinity for SOC. Therefore, global surface soils have been recognized to serve as an important reservoir for POPs, representing an integration of several processes over a timescale of years to decades (Sweetman *et al.*, 2005). While the importance of soil biogeochemistry and the role of SOC was recognized some 30 years ago (Karickhoff *et al.*, 1979), it is only in the past decade that organic carbon has been recognized as the key parameter governing spatial variability of POPs in soils (Cousins *et al.*, 1999) and partitioning in the marine environment (Lohmann *et al.*, 2005). It is, therefore, conceivable that biochars in soils, due to their high sorption capacity (see Section 3), can potentially serve as sinks for POPs and significantly influence the process of "grasshopping" and their global distribution (Fig. 1). The work of Meijer *et al.* (2002) has highlighted the likelihood of a much retarded transport due to strong sorption to SOC than what has been taken into account in predictions so far. In recent years, several workers have called for a greater understanding and accounting of role of SOC in fluxes, distributions, and long-range transport of organic contaminants (Koblickova *et al.*, 2008; Lohmann *et al.*, 2007; Scheringer, 2009). If soil application of biochars becomes a common practice, the distribution of POPs may be altered even more and may require understanding of the potential impact of the biochar applications to soil on the accumulation and distribution of POPs.

Biochar particles can potentially serve as the vehicles for off-site transport of agrochemicals. The importance of colloidal transport as a pathway of off-site migration of relatively hydrophobic contaminants is well recognized (McCarthy and Zachara, 1989). It is also known that colloids (being richer in organic matter and greater sorption affinity) often get enriched in contaminants (such as nutrients and pesticides) during their overland transport (Rose and Dalal, 1988; Sharpley and Menzel, 1987). Soil application of biochar may facilitate increased off-site migration of agrochemicals through at least two mechanisms: (i) due to their low specific gravity the freshly

produced biochar particles are erosion prone and are likely to get easily entrained in surface runoff, and (ii) the extraordinary ability of biochars to sorb chemicals is likely to lead to a greater "enrichment" of residue on the colloids during their transport. However, whether these contaminants would remain bioavailable to potentially exert an effect on organisms in the receiving environment, is not clear.

5.5. Ecotoxicological effect on soil organisms

A variety of organic compound including bio-oils, ash, pyroligneous acids (Steiner *et al.*, 2008), and volatile matter (McClellan *et al.*, 2007) may remain on biochar surfaces immediately following pyrolysis. However, the fate of these compounds with time in soil after biochar application is unknown. It is expected that the water-soluble components such as acids, alcohols, aldehydes, ketones, and sugars that are easily metabolized by soil microbes may have a positive effect. Whereas the presence of compounds such as PAHs, cresols, xylenols, formaldehyde, acrolein, and other toxic carbonyl compounds (depending on pyrolysis conditions) may have bactericidal or fungicidal activity (Painter, 2001). Some of the effects of biochar application on soil microbial changes have already been discussed in Section 5.

Earthworms are useful indicators of soil health (Paoletti *et al.*, 1998), as they are highly mobile and sensitive to soil contamination (Yeardley *et al.*, 1996). Several studies have tested the impacts of biochar on earthworms using either mortality or avoidance behavior studies. For example, Wen *et al.* (2009) spiked three soils with pentachlorophenol (PCP) in the laboratory and included one field-contaminated soil, which was then amended with 2.0% biochar, humic acid, and peat and aged for either 7 or 250 days. They noted that the bioavailability and the bioaccumulation factor of PCP for earthworms (*Eisenia fetida*) were significantly reduced by biochar amendment to the studied soils. This is consistent with the ability of biochar to sorb organic contaminants, as discussed above (Section 3). Also, as mentioned above, Cu contents of some poultry biochars have been found to be as high as 1000 mg/kg (Gaskin *et al.*, 2008). Earthworms can exhibit sublethal toxic responses at relatively low concentrations (< 34 mg/kg) of Cu in soil (Helling *et al.*, 2000; Van Zwieten *et al.*, 2004), and, therefore, care must be taken in the soil application to avoid the accumulation of toxic levels of Cu. Biochar may also indirectly influence the soil environment for earthworms. It has also been suggested that increasing pH of acid soils through the application of charcoal can benefit earthworm population (Chan *et al.*, 2008; Topoliantz and Ponge, 2005; Van Zwieten *et al.*, 2010a). However, alkaline biochars if applied at high rates can also adversely affect the soil environmental conditions (pH, EC) for earthworms (Liesch *et al.*, 2010). Longer-term studies on a range of biochars and soil health have already been called for by several workers (Pietikäinen *et al.*, 2000; Warnock *et al.*, 2007).

6. Knowledge Gaps and Research Needs

The review of the literature, especially dealing with agronomic and environmental implications of biochar application to soils, has highlighted several benefits as well as potentially negative implications, such as (i) reduced efficacy and increased agro-input costs, (ii) release and increased persistence of agrochemicals, (iii) accumulation and transport of contaminants, and (iv) potential ecotoxicological impacts on soil flora and fauna. Several knowledge gaps have emerged, as listed below. These are, by no means, intended to cover all aspects of future research on biochar applications to soils, instead highlight key gaps that need to be addressed especially to avoid potential unintended consequences identified in this chapter.

- Biochar properties are a function of type of feedstock and pyrolytic conditions employed in its production. Given the variety of feedstock being used and different production technologies employed, high heterogeneity in biochar properties has been observed. Studies on limited ranges of biochars prepared at different temperatures have shown marked differences in their properties and ability to supply nutrients, immobilize, or interact with chemicals such as herbicides and heavy metals. Despite the increasing research effort in recent years in this area, a sound understanding of the relationship between desired biochar characteristics and production conditions/feedstock is still lacking. Further work is needed, especially to identify what combination of feedstock and pyrolysis conditions would provide the most appropriate properties for biochar as a soil amendment.
- Due to the extraordinary ability of biochars to sorb organic chemicals, one of the major unintended consequences of biochar application to soil identified in this chapter is the likely compromised efficacy of pesticides. Owing to the direct and indirect agronomic and economic implications associated with this finding, it is imperative that a thorough understanding is developed about the nature and extent of such effects of different types of biochars in soils. Perhaps the most important questions here are as follows: (i) Over time will biochar in soil retain or lose its ability to deactivate herbicides? (ii) Could biochars production be customized, or be pretreated before application or are applied to soil in a manner to avoid such adverse effects (e.g., by incorporation, banding, or subsurface placement)?
- Once applied to soil, biochars undergo numerous biogeochemical interactions that are likely to affect their properties over time. Most studies in the literature are on freshly prepared biochars. The understanding of organomineral interactions of biochar in soils and consequences of aged biochars for pesticide, nutrient, and microbiological interactions is extremely limited. This aspect deserves urgent scientific attention.

- The questions commonly asked by regulators and community about biochars as a source of contaminants and their long-term impact on natural resources have not been answered yet. Limited published/unpublished work on biochars sourced from plant biomass or crop residue so far indicates that contaminants such as PAHs, dioxins may not be a major issue (in relation to existing guidelines on soil contaminants). However, some biochars have been noted to contain elevated levels of heavy metals and may also contain precursors of toxicants that may be created during biochar production. Currently, there is no comprehensive study available in the literature that can address the above questions adequately, especially for biochars produced from wastes.
- This chapter has shown that effects of biochar on soil flora and fauna are poorly understood. Given that residues of some of the potentially toxicants (e.g., heavy metals, PAHs, cresols, xylenols, formaldehyde, acrolein, and other toxic carbonyl compounds) may remain on biochars (depending on pyrolysis conditions), their ecotoxicological impact on plants, microorganisms, and other indicators of soil health (e.g., earthworms) need to be established. The little work cited above clearly calls for further investigations in this area.
- Particles of freshly made biochars, being relatively lighter than other soil particles, are likely to be easily transported in surface runoff water. Better understanding is needed of the role of biochar-assisted transport and off-site migration of pesticides and other contaminants. Moreover, any environmental effects of biochar-sorbed contaminants on nontarget organisms in receiving environments need to be assessed. If biochar addition to soil becomes as a widely adopted agronomic practice, the potential impact this may have on accumulation of POPs in soils and their long-range transport would need to be evaluated.
- As the use of biochar in soils becomes common, the potential impact on quality of produce may also become important, especially those targeting a particular market niche. To the best of our knowledge, currently, no work is available in the literature on this topic.

Undoubtedly, biochar application to soil has major potential benefits in relation to carbon sequestration, bioenergy, enhanced soil fertility, and waste management (as discussed above and reviewed previously by several workers). However, prior to recommendation of this agronomic practice at a large scale, a complete analysis of potential agronomic and environmental implications is prudent. This chapter has highlighted that while the body of the literature on biochar interactions in soil and environment is growing rapidly, some of the potential unintended consequences have not been fully appreciated or addressed as yet. A better understanding of long-term agronomic and environmental impact of biochar application to soils is essential for the realization of full potential and sustainability of the biochar technology.

ACKNOWLEDGMENTS

The authors thank CSIRO's Sustainable Agriculture Research Flagship for the financial support and the two internal reviewers (Drs. Michael Warne and Mark Farrell) for their comments on the chapter.

REFERENCES

Abelmann, K., Kleineidam, S., Knicker, H., Grathwohl, P., and Kögel-Knabner, I. (2005). Sorption of HOC in soils with carbonaceous contamination: Influence of organic-matter composition. *J. Plant Nutr. Soil Sci.* **168,** 1–14.

Accardi-Dey, A., and Gschwend, P. M. (2003). Reinterpreting literature sorption data considering both absorption into organic carbon and adsorption onto black carbon. *Environ. Sci. Technol.* **37,** 99–106.

Ahangar, A. G., Smernik, R. J., Kookana, R. S., and Chittleborough, D. J. (2008). Separating the effects of organic matter-mineral interactions and organic matter chemistry on the sorption of diuron and phenanthrene. *Chemosphere* **72,** 886–890.

Ahmad, R., Kookana, R. S., Alston, A. M., and Skjemstad, J. O. (2001). The nature of soil organic matter affects the sorption of pesticides. 1. Relationship with carbon chemistry as determined by ^{13}C CPMAS NMR spectroscopy. *Environ. Sci. Technol.* **35,** 878–884.

Alexander, M. (1995). How toxic are toxic chemicals in soil? *Environ. Sci. Technol.* **29,** 2713–2717.

Allen-King, R. M., Grathwohl, P., and Ball, W. P. (2002). New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments and rocks. *Adv. Water Resour.* **25,** 985–1016.

Alleoni, L. R. F., Cambri, M. A., Caires, E. F., and Garbuio, F. J. (2010). Acidity and aluminum speciation as affected by surface liming in tropical no-till soils. *Soil Sci. Soc. Am. J.* **74,** 1010–1017.

Almendros, G., González-Vila, F. J., and Martin, F. (1990). Fire-induced transformation of soil organic matter from an oak forest. An experimental approach to the effects of fire on humic substances. *Soil Sci.* **149,** 158–168.

Atkinson, C. J., Fitzgerald, J. D., and Hipps, N. A. (2010). Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: A review. *Plant Soil* **337,** 1–18.

Baggs, E. M. (2008). A review of stable isotope techniques for N2O source partitioning in soils: Recent progress, remaining challenges and future considerations. *Rapid Commun. Mass Spectrom.* **22,** 1664–1672.

Baldock, J. A., and Smernik, R. J. (2002). Chemical composition and bioavailability of thermally altered *Pinus resinosa* (red pine) wood. *Org. Geochem.* **33,** 1093–1109.

Barton, S. S., Evans, M. J. B., Halliop, E., and MacDonald, J. A. F. (1997). Acidic and basic sites on the surface of porous carbon. *Carbon* **35,** 1361–1366.

Biniak, S., Szymanski, G., Siedlewski, J., and Swiatkowski, A. (1997). The characterization of activated carbons with oxygen and nitrogen surface groups. *Carbon* **35,** 1799–1810.

Boehm, H. P. (2002). Surface oxides on carbon and their analysis: A critical assessment. *Carbon* **40,** 145–149.

Bornemann, L. C., Kookana, R. S., and Welp, G. (2007). Differential sorption behaviour of aromatic hydrocarbons on charcoals prepared at different temperatures from grass and wood. *Chemosphere* **67,** 1033–1042.

Bracmort, K. S. (2009). Biochar: Examination of an emerging concept to mitigate climate change., http://ncseonline.org/NLE/CRs/abstract.cfm?NLEid=2216, Congressional Research Service, 7–5700, CRS report no. R40186.
Bridle, T. R., and Pritchard, D. (2004). Energy and nutrient recovery from sewage sludge via pyrolysis. *Water Sci. Technol.* **50,** 169–175.
Brown, R. A., Kercher, A. K., Nguyen, T. H., Nagle, D. C., and Ball, W. P. (2006). Production and characterization of synthetic wood chars for use as surrogates for natural sorbents. *Org. Geochem.* **37,** 321–333.
Bucheli, T. D., and Gustafsson, O. (2003). Soot sorption of non-ortho and ortho substituted PCBs. *Chemosphere* **53,** 515–522.
Budinova, T. K., Gergova, K. M., Petrov, N. V., and Minkova, V. N. (1994). Removal of metal ions from aqueous solution by activated carbons obtained from different raw materials. *J. Chem. Technol. Biotechnol.* **60,** 177–182.
Cao, X., Ma, L., Gao, B., and Harris, W. (2009). Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environ. Sci. Technol.* **43,** 3285–3291.
Chagger, H. K., Kendall, A., McDonald, A., Pourkashanian, M., and Williams, A. (1998). Formation of dioxins and other semi-volatile compounds in biomass combustion. *Appl. Energy* **60,** 101–114.
Chan, K. Y., and Xu, K. (2009). Biochar: Nutrient properties and their enhancement. *In* "Biochar for Environmental Management. Science and Technology" (J. Lehmann and S. Joseph, Eds.), pp. 13–323. Earthscan, London.
Chan, K. Y., Van Zwieten, L., Meszaros, I., Downie, A., and Joseph, S. (2007). Agronomic values of greenwaste biochar as a soil amendment. *Aust. J. Soil Res.* **45,** 629–634.
Chan, K. Y., Van Zwieten, L., Meszaros, I., Downie, A., and Joseph, S. (2008). Using poultry litter biochars as soil amendments. *Aust. J. Soil Res.* **46,** 437–444.
Chen, G., Yu, Q., and Sjostrom, K. (1997). Reactivity of char from pyrolysis of birchwood. *J. Anal. Appl. Pyrolysis* **40–41,** 491–499.
Chen, J., Zhu, D., and Sun, C. (2007). Effect of heavy metals on the sorption of hydrophobic organic compounds to wood charcoal. *Environ. Sci. Technol.* **41,** 2536–3541.
Cheng, C. H., Lehmann, J., Thies, J. E., Burton, S. D., and Engelhard, M. H. (2006). Oxidation of black carbon by biotic and abiotic processes. *Org. Geochem.* **37,** 1477–1488.
Cheng, C. H., Lehmann, J., and Engelhard, M. H. (2008). Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. *Geochim. Cosmochim. Acta* **72,** 1598–1610.
Chiou, C. T., Porter, P. E., and Schmeddling, D. W. (1983). Partition equilibria of nonionic organic compounds between soil organic matter and water. *Environ. Sci. Technol.* **17,** 227–231.
Chun, Y., Sheng, G. Y., Chiou, C. T., and Xing, B. S. (2004). Compositions and sorptive properties of crop residue-derived chars. *Environ. Sci. Technol.* **38,** 4649–4655.
Clough, T. J., Bertram, J. E., Ray, J. L., Condron, L. M., O'Callaghan, M., Sherlock, R. R., and Wells, N. S. (2010). Unweathered wood biochar impact on nitrous oxide emissions from a bovine-urine amended pasture soil. *Soil Sci. Soc. Am. J.* **74,** 852–860.
Cousins, I. T., Gevao, B., and Jones, K. C. (1999). Measuring and modelling the vertical distribution of semivolatile organic compounds in soils. I: PCB and PAH soil core data. *Chemosphere* **39,** 2507–2518.
D'Emeden, F. H., and Llewellyn, R. S. (2006). No-tillage adoption decisions in southern Australian cropping and the role of weed management. *Aust. J. Exp. Agric.* **46,** 563–569.
DeLuca, T. H., MacKenzie, M. D., and Gundale, M. J. (2009). Biochar effects on soil nutrient transformations. *In* "Biochar for Environmental Management: Science and Technology" (J. Lehmann and S. Joseph, Eds.), Earthscan, London.

Downie, A., Crosky, A., and Munroe, P. (2009). Physical properties of biochar. *In* "Biochar for Environmental Management: Science and Technology" (J. Lehmann and S. Joseph, Eds.), Earthscan, London.
Downie, A., Munroe, P., Cowie, A., Van Zwieten, L., and Lau, D. M. S. (2011). Biochar as a Geo-Engineering climate solution: Hazard identification and risk management. *Crit. Rev. Environ. Sci. Technol.*10.1080/10643389.2010.507980, (in press).
Figueiredo, J. L., Pereira, M. F. R., Freitas, M. M. A., and Órfão, J. J. M. (1999). Modification of the surface chemistry of activated carbons. *Carbon* **37,** 1379–1389.
Gaskin, J. W., Steiner, C., Harris, K., Das, K. C., and Bibens, B. (2008). Effect of low temperature pyrolysis conditions on biochars for agricultural use. *Trans. ASABE* **51,** 2061–2069.
Glaser, B., Haumaier, L., Guggenberger, G., and Zech, W. (2001). The 'Terra Preta' phenomenon: A model for sustainable agriculture in the humid tropics. *Naturwissenschaften* **88,** 37–41.
Glaser, B., Lehmann, J., and Zech, W. (2002). Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal: A review. *Biol. Fertil. Soils* **35,** 219–230.
Glaser, B., Parr, M., Braun, C., and Kopolo, G. (2009). Biochar is carbon negative. *Nat. Geosci.* **2**(1), 2.
Gundale, M. J., and DeLuca, T. H. (2006). Temperature and source material influence ecological attributes of ponderosa pine and Douglas fir charcoal. *For. Ecol. Manage.* **231,** 86–93.
Hamer, U., Marschner, B., Brodowski, S., and Amelung, W. (2004). Interactive priming of black carbon and glucose mineralisation. *Org. Geochem.* **35,** 823–830.
Hammes, K., and Schmidt, M. W. I. (2009). Changes of biochar in soil. *In* "Biochar for Environmental Management: Science and Technology" (J. Lehmann and S. Joseph, Eds.), Earthscan, London.
Helling, B., Reinecke, S. A., and Reinecke, A. J. (2000). Effects of the fungicide copper oxychloride on the growth and reproduction of Eisenia fetida (Oligochaeta). *Ecotoxicol. Environ. Safe.* **46,** 108–116.
Huang, C. P. (1978). Chemical interactions between inorganic and activated carbon. *In* "Carbon Adsorption Handbook" (P. N. Cheremisinoff and F. Ellerbursch, Eds.), pp. 281–330. Ann Arbor Science, New York.
Huang, W. L., Peng, P. A., Yu, Z. Q., and Fu, J. M. (2003). Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments. *Appl. Geochem.* **18,** 955–972.
Hunter, W. H., Gan, J., and Kookana, R. S. (2010). Bioavailability of hydrophobic organic contaminants in soils and sediments. *In* "Biophysico-Chemical Processes of Anthropogenic Organic Compounds in Environmental Systems" (P. M. Huang and N. Senesi, Eds.), John Wiley & Sons, Hoboken, NJ, (in press).
James, G., Sabatini, D. A., Chiou, C. T., Rutherford, D., Scott, A. C., and Karapanagioti, H. K. (2005). Evaluating phenanthrene sorption on various wood chars. *Water Res.* **39,** 549–558.
Jia, Y. T., Xiao, B., and Thomas, K. M. (2002). Adsorption of metal ions on nitrogen surface functional groups in activated carbon. *Langmuir* **18,** 470–478.
Jin, H., Lehmann, J., and Thies, J. E. (2008). Soil microbial community response to amending corn soils with corn stover charcoal. *In* "Proceedings of the 2008 Conference of International Biochar Initiative," 8–10 September 2008, Newcastle, UK.
Jonker, M. T. O., Hawthorne, S. B., and Koelmans, A. A. (2005). Extremely slowly desorbing polycyclic aromatic hydrocarbons from soot and soot-like materials: Evidence by supercritical fluid extraction. *Environ. Sci. Technol.* **39,** 7889–7895.

Joseph, S. D., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C. H., Hook, J., Van Zwieten, L., Kimber, S., Cowie, A., Singh, B. P., Lehmann, J., and Foidl, N. (2010). An investigation into the reactions of biochar in soil. *Aust. J. Soil Res.* **48,** 501–515.

Karickhoff, S. W., Brown, D. S., and Scott, T. A. (1979). Sorption of hydrophobic pollutants on natural sediments. *Water Res.* **13,** 241–248.

Keller, M. L., Masiello, C. A., Dugan, B., Rudgers, J. A., and Capareda, S. C. (2010). Phytotoxicity and plant productivity analysis of tar-enriched biochars. *In* "American Geophysical Union, Fall Meeting 2008, abstract #B23D-0481," http://adsabs.harvard.edu/abs/2008AGUFM.B23D0481K, (accessed October 5, 2010).

Killops, S. D., and Killops, V. J. (2005). An Introduction to Organic Geochemistry.2nd edn. Blackwell Publishing, Malden.

Kleineidam, S., Rügner, H., and Grathwohl, P. (1999). Impact of grain scale heterogeneity on slow sorption kinetics. *Environ. Toxicol. Chem.* **18,** 1673–1678.

Koblickova, M., Ruzickova, P., Cupr, P., Komprda, J., Holoubek, I., and Klanova, J. (2008). Soil burdens of persistent organic pollutants: Their levels, fate, and risks. Part IV. Quantification of volatilization fluxes of organochlorine pesticides and polychlorinated biphenyls from contaminated soil surfaces. *Environ. Sci. Technol.* **43,** 3588–3595.

Kookana, R. S. (2010). The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: A review. *Aust. J. Soil Res.* **48,** 627–637.

Krull, E. S., Baldock, J. A., Skjemstad, J. O., and Smernik, R. S. (2009). Characteristics of biochar: Organo-chemical properties. *In* "Biochar for Environmental Management: Science and Technology" (J. Lehmann and S. Joseph, Eds.), Earthscan, London.

Kwapinski, W., Byrne, C. M. P., Kryachko, E., Wolfram, P., Adley, C., Leahy, J. J., Novotny, E. H., and Hayes, M. H. B. (2010). Biochar from biomass and waste. *Waste Biomass Valorization* **1,** 177–189.

Laird, A. D. (2008). The charcoal vision. A win-win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. *Agron. J.* **100,** 178–181.

Lehmann, J. (2007a). Bio-energy in the black. *Front. Ecol. Environ.* **5,** 381–387.

Lehmann, J. (2007b). A handful of carbon. *Nature* **447,** 143–144.

Lehmann, J., and Joseph, S. (2009). Biochar for environmental management: An introduction. *In* "Biochar for Environmental Management: Science and Technology" (J. Lehmann and S. Joseph, Eds.), Earthscan, London.

Lehmann, J., da Silva, J. P. Jr., Steiner, C., Nehls, T., Zech, W., and Glaser, B. (2003). Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol in the Central Amazon basin: Fertiliser, manure and charcoal amendments. *Plant Soil* **249,** 343–357.

Lehmann, J., Gaunt, J., and Rondon, M. (2006). Bio-char sequestration in terrestrial ecosystems—A review. *Mitig. Adapt. Strateg. Glob. Change* **11**(2), 403–427.

Liang, B. (2008). The Biogeochemistry of Black Carbon in Soils. PhD thesis, Cornell University, Ithaca, NY.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J. O., Thies, J., Luizaö, F. J., Petersen, J., and Neves, E. G. (2006). Black carbon increases cation exchange capacity in soils. *Soil Sci. Soc. Am. J.* **70,** 1719–1730.

Liesch, A. M., Weyers, S. L., Gaskin, J. W., and Das, K. C. (2010). Impact of two different biochars on earthworm growth and survival. *Ann. Environ. Sci.* **4,** 1–9.

Loganathan, V. A., Feng, Y., Sheng, G. D., and Clement, T. P. (2009). Crop-residue-derived char influences sorption, desorption and bioavailability of atrazine in soils. *Soil Sci. Soc. Am. J.* **73,** 967–974.

Lohmann, R., Mac Farlane, J. K., and Gschwend, P. M. (2005). Importance of black carbon to sorption of native PAHs, PCBs, and PCDDs in Boston and New York harbour sediments. *Environ. Sci. Technol.* **39,** 141–148.

Lohmann, R., Breivik, K., Dachs, J., and Muir, D. (2007). Global fate of POPs: Current and future research directions. *Environ. Pollut.* **150,** 150–165.
Luthy, R. G., Aiken, G. R., Brusseau, M. L., Cunningham, S. D., Gschwend, P. M., Pignatello, J. J., Reinhard, M., Traina, S. J., Weber, W. J., and Westall, J. C. (1997). Sequestration of hydrophobic organic contaminants by geosorbents. *Environ. Sci. Technol.* **31,** 3341–3347.
Major, J., Lehmann, J., Rondon, M., and Goodale, C. (2009). Fate of soil applied black carbon: Downward migration, leaching and soil respiration. *Glob. Change Biol.* **16,** 1366–1379.
Mathews, J. A. (2008). Viewpoint: Carbon-negative biofuels. *Energy Policy* **36**(3), 940–945.
McBeath, A. V., and Smernik, R. J. (2009). Variation in the degree of aromatic condensation of chars. *Org. Geochem.* **40,** 1161–1168.
McCarthy, J. F., and Zachara, J. M. (1989). Subsurface transport of contaminants. *Environ. Sci. Technol.* **23,** 496–502.
McClellan, A. T., Deenik, J., G., and Antal, M. (2007). Effects of flash carbonized macadamia nutshell charcoal on plant growth and soil chemical properties.American Society of Agronomy Abstracts, 3–7 November, New Orleans, LA.
Meijer, S. N., Steinnes, E., Ockenden, W. A., and Jones, K. C. (2002). Influence of environmental variables on the spatial distribution of PCBs in Norwegian and U.K. soils: Implications for global cycling. *Environ. Sci. Technol.* **36,** 2146–2153.
Mohan, D., Pittman, C. U. Jr., Brcika, M., Smith, F., Yancey, B., Mohammad, J., Steele, P. H., Alexandre-Franco, M. F., Gómez-Serrano, V., and Gong, H. (2007). Sorption of arsenic, cadmium and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *J. Colloid Interface Sci.* **310,** 57–73.
Montes-Morán, M. A., Suárez, D., Menéndez, J. A., and Fuente, E. (2004). On the nature of basic sites on carbon surfaces: An overview. *Carbon* **42,** 1219–1225.
Nam, K., and Alexander, M. (1998). Role of nanoporosity and hydrophobicity in sequestration and bioavailability: Tests with model solids. *Environ. Sci. Technol.* **32,** 71–74.
Namgay, T., Singh, B., and Singh, B. P. (2010). Influence of biochar application to soil on the availability of As, Cd, Cu, Pb, and Zn to maize (*Zea mays* L.). *Aust. J. Soil Res.* **48,** 638–647.
NEPM. (1999). National Environment Protection (Assessment of Site Contamination) Measure 1999. National Environment Protection Council, Adelaide, South Australia.
Neve, P., and Powles, S. B. (2005). Recurrent selection with reduced herbicide rates results in the rapid evolution of herbicide resistance in Lolium rigidum. *Theor. Appl. Genet.* **110,** 1154–1166.
Nguyen, B. T., and Lehmann, J. (2009). Black carbon decomposition under varying water regimes. *Org. Geochem.* **35,** 823–830.
Novak, J. M., Busscher, W. J., Laird, D. L., Ahmedna, M., Watts, D. W., and Niandou, M. A. S. (2009). Impact of biochar amendment on fertility of a Southeastern Coastal Plain. *Soil Sci.* **174,** 105–112.
NRMMC. (2004). Guidelines for Sewerage Systems—Biosolids Management.National Water Quality Management Strategy Paper No 13, National Resource Management Ministers Council, Canberra, Australia, p. 45.
NSW EPA. (1997). Guidelines for the Use and Disposal of Biosolids Products New South Wales Environment Protection Authority, Sydney.
NSW EPA. (1997). EPA Compost Guidelines (Public Consultation) New South Wales Environment Protection Authority, Sydney.
Ogawa, M., Okimori, Y., and Takahashi, F. (2006). Carbon sequestration by carbonization of biomass and forestation: Three case studies. *Mitig. Adapt. Strateg. Glob. Change* **11,** 429–444.

Painter, T. J. (2001). Carbohydrate polymers in food preservation: An integrated view of the Maillard reaction with special reference to discoveries of preserved foods in Sphagnum dominated peat bogs. *Carbohydr. Polym.* **36,** 335–347.
Paoletti, M. G., Sommaggio, D., Favretto, M. R., Petruzzelli, G., Pezzarossa, B., and Barbafieri, M. (1998). Earthworms as useful bioindicators of agroecosystem sustainability in orchards and vineyards with different inputs. *Appl. Soil Ecol.* **10,** 137–150.
Pietikäinen, J., Kiikkilä, O., and Fritze, H. (2000). Charcoal as a habitat for microbes and its effect on the microbial community of the underlying humus. *Oikos* **89,** 231–242.
Pignatello, J. J., Kwon, S., and Lu, Y. F. (2006). Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): attenuation of surface activity by humic and fulvic acids. *Environ. Sci. Technol.* **40,** 7757–7763.
Powles, S. B., Preston, C., Bryan, I. B., and Jutsum, A. R. (1996). Herbicide resistance: Impact and Management. *Adv. Agron.* **58,** 57–93.
Preston, C. M., and Schmidt, M. W. I. (2006). Black (pyrogenic) carbon: A synthesis of current knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences* **3,** 397–420.
Rogovska, N., Laird, D., Cruse, R., and Heaton, E. (2010). Evaluation of biochar quality utilizing standard germination test. *In* "Proceedings of the ASA, CSSA and SSSA 2010 International Annual Meeting, Long Beach, CA, October 31–November 4. Presentation No. 166–4," http://a-c-s.confex.com/crops/2010am/webprogram/Paper57931.htmlAccessed October 5, 2010.
Rondon, M. A., Lehmann, J., Ramírez, J., and Hurtado, M. (2007). Biological nitrogen fixation by common beans (*Phaseolus vulgaris* L.) increases with bio-char additions. *Biol. Fertil. Soils* **43,** 699–708.
Rose, C. W., and Dalal, R. C. (1988). Erosion and runoff of nitrogen. *In* "Advances in Nitrogen Cycling in Agricultural Ecosystems" (J. R. Wilson, Ed.). CAB International, Wallingford.
Sarmah, A. K., Srinivasan, P., Smernik, R. J., Manley-Harris, M., Antal, M. J. Jr., Downie, A., and Van Zwieten, L. (2010). Retention capacity of biochar-amended New Zealand dairy farm soil for an estrogenic steroid hormone and its primary metabolite. *Aust. J. Soil Res.* **48,** 648–658.
Scheringer, M. (2009). Long-range transport of organic chemicals in the environment. *Environ. Toxicol. Chem.* **28,** 677–690.
Schmidt, M. W. I., and Noack, A. G. (2000). Black carbon in soils and sediments: Analysis, distribution, implications and current challenges. *Glob. Biogeochem. Cycle* **14,** 777–793.
Semple, K. T., Morriss, A. W. J., and Paton, G. I. (2003). Bioavailability of hydrophobic organic contaminants in soils: Fundamental concepts and techniques for analysis. *Eur. J. Soil Sci.* **54,** 809–818.
Sharpley, A. N., and Menzel, R. G. (1987). The impact of soil and fertilizer phosphorus on the environment. *Adv. Agron.* **41,** 297–324.
Sheng, G. Y., Yang, Y. N., Huang, M. S., and Yang, K. (2005). Influence of pH on pesticide sorption by soil containing wheat residue-derived char. *Environ. Pollut.* **134,** 457–463.
Sinclair, K., Slavich, P., Morris, S., Kimber, S., Downie, A., and Van Zwieten, L. (2010). Influence of biochar on soil fertility, carbon storage and biomass in subtropical pasture: Results from a 3 year field study. *In* "Proceedings of the 3rd International Biochar Conference, Rio de Janeiro, Brazil, 12–15 September 2010," pp. 169–170.
Singh, B., and Heffernan, S. (2002). Layer charge characteristics of smectites from Vertosols (Vertisols) of New South Wales. *Aust. J. Soil Res.* **40,** 1159–1170.
Singh, N., and Kookana, R. S. (2009). Organo-mineral interactions mask the true sorption potential of biochars in soils. *J. Environ. Sci. Health B* **44,** 214–219.

Singh, B. P., Hatton, B. J., Singh, B., Cowie, A. L., and Kathuria, A. (2010a). Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. *J. Environ. Qual.* **39**(4), 1224–1235.

Singh, B., Singh, B. P., and Cowie, A. L. (2010b). Characterisation and evaluation of biochars for their application as a soil amendment. *Aust. J. Soil Res.* **48,** 516–525.

Smernik, R. J., Kookana, R. S., and Skjemstad, J. O. (2006). NMR characterization of 13C-Benzene sorbed to natural and prepared charcoals. *Environ. Sci. Technol.* **40,** 1764–1769.

Sohi, S. P., Krull, E., Lopez-Capel, E., and Bol, R. (2010). A review of biochar and its use and function in soil. *Adv. Agron.* **105,** 47–82.

Solaiman, Z. M., Blackwell, P., Abbott, L. K., and Storer, P. (2010). Direct and residual effect of biochar application on mycorrhizal root colonisation, growth and nutrition of wheat. *Aust. J. Soil Res.* **48,** 546–554.

Spokas, K. A., Koskinen, W. C., Baker, J. M., and Reicosky, D. C. (2009). Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides on Minnesota soil. *Chemosphere* **77,** 574–581.

Steinbeiss, S., Gleixner, G., and Antonietti, M. (2009). Effect of biochar amendment on soil carbon balance and soil microbial activity. *Soil Biol. Biochem.* **41,** 1301–1310.

Steiner, C., Teixeira, W. G., Lehmann, J., Nehls, T., de Macedo, J. L. V., Blum, W. E. H., and Zech, W. (2007). Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. *Plant Soil* **291,** 275–290.

Steiner, C., Das, K. C., Garcia, M., Forster, B., and Zech, W. (2008). Charcoal and smoke extract stimulate the soil microbial community in a highly weathered xanthic Ferralsol. *Pedobiologia* **51,** 359–366.

Sweetman, A. J., Valle, M. D., Prevedouros, K., and Jones, K. C. (2005). The role of soil organic carbon in the global cycling of persistent organic pollutants (POPs): Interpreting and modelling field data. *Chemosphere* **60,** 959–972.

Thies, E., and Rilling, M. C. (2009). Characteristics of biochar: Biological properties. *In* "Biochar for Environmental Management. Science and Technology" (J. Lehmann and S. Joseph, Eds.), Earthscan, London.

Topoliantz, S., and Ponge, J. F. (2005). Charcoal consumption and casting activity by *Pontoscolex corethrurus* (Glossoscolecidae). *Appl. Soil Ecol.* **28,** 217–224.

Toth, J., and Milham, P. J. (1975). Activated-carbon and ash-carbon effects on the adsorption and phytotoxicity of diuron. *Weed Res.* **15,** 171–176.

Toth, J., Milham, P. J., and Raison, J. M. (1981). Ash from rice stubble inactivates thiobencarb and molinate. *Weed Res.* **21,** 113–117.

Toth, J., Milham, P. J., and Kaldor, C. J. (1999). Decreased phytotoxicity of diuron applied over ash of recently burned kangaroo grass (*Themeda australis* (R.Br.) Stapf). *Plant Prot. Quart.* **14,** 151–154.

Treseder, K. K. (1998). A meta-analysis of mycorrhizal responses to nitrogen, phosphorus, and atmospheric CO_2 in field studies. *Commun. Soil Sci. Plant Anal.* **29,** 1779–1784.

Uchimiya, M., Lima, I. M., Klasson, K. T., and Wartelle, L. H. (2010a). Contaminant immobilization and nutrient release by biochar soil amendment: Roles of natural organic matter. *Chemosphere* **80,** 935–940.

Uchimiya, M., Lima, I. M., Klasson, K. T., Chang, S., Wartelle, L. H., and Rodgers, J. E. (2010b). Immobilization of heavy metal ions (CuII, CdII, NiII, and PbII) by broiler litter-derived biochars in water and soil. *J. Agric. Food Chem.* **58,** 5538–5544.

Van Noort, P. C. M., Cornelissen, G., ten Hulscher, T. E. M., Vrind, B. A., Rigterink, H., and Belfroid, A. C. (2003). Slow and very slow desorption of organic compounds from sediment: Influence of sorbate planarity. *Water Res.* **37,** 317–2322.

Van Zwieten, L., Rust, J., Kingston, T., Merrington, G., and Morris, S. (2004). Influence of copper fungicide residues on occurrence of earthworms in avocado orchard soils. *Sci. Total Environ.* **329,** 29–41.

Van Zwieten, L., Singh, B. P., Joseph, S., Kimber, S., Cowie, A., and Chan, K. Y. (2009). Biochar reduces emissions of non-CO_2 GHG from soil. *In* "Biochar for Environmental Management" (J. Lehmann and S. Joseph, Eds.), Earthscan, London.

Van Zwieten, L., Kimber, S., Morris, S., Chan, Y. K., Downie, A., Rust, J., Joseph, S., and Cowie, A. (2010a). Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant Soil* **327,** 235–246.

Van Zwieten, L., Kimber, S., Morris, S., Downie, A., Berger, E., Rust, J., and Scheer, C. (2010b). Influence of biochars on flux of N_2O and CO_2 from Ferrosol. *Aust. J. Soil Res.* **48,** 555–568.

Van Zwieten, L., Kimber, S., Downie, A., Morris, S., Rust, J., and Chan, K. Y. (2010c). A glasshouse study on the interaction of low mineral ash biochar with nitrogen in a sandy soil. *Aust. J. Soil Res.* **48,** 569–576.

Vassilev, S. V., and Braekman-Danheux, C. (1999). Characterization of refuse-derived char from municipal solid waste. 2. Occurrence, abundance and source of trace elements. *Fuel Process. Technol.* **59,** 135–161.

Verheijen, F., Jeffery, S., Bastos, A. C., van der Velde, M., and Diafas, F. (2010). Biochar application to soils. A critical scientific review of effects on soil properties, processes, and functions.EUR 24099 EN Office for the Official Publications of the European Communities, Luxembourgp. 149.

Wania, F. (2006). Potential of degradable organic chemicals for absolute and relative enrichment in the Arctic. *Environ. Sci. Technol.* **40,** 569–577.

Warnock, D. D., Lehmann, J., Kuyper, T. W., and Rillig, M. C. (2007). Mycorrhizal responses to biochar in soil—Concepts and mechanisms. *Plant Soil* **300,** 9–20.

Weber, W. J. Jr., Mcglnley, P. M., and Katz, L. E. (1992). A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessment. *Environ. Sci. Technol.* **26,** 1955–1962.

Wen, B., Li, R. J., Zhang, S., Shan, X. Q., Fang, J., Xiao, K., and Khan, S. U. (2009). Immobilization of pentachlorophenol in soil using carbonaceous material amendments. *Environ. Pollut.* **157,** 968–974.

Weyers, S. L., Gaskin, J., Liesch, A. M., and Das, K. C. (2010). Earthworms, microbes and the release of c and n in biochar amended soil. *In* "Proceedings of the 2010 U.S. Biochar Initiative Conference, June 27–30, 2010, Ames, Iowa" .

Winsley, P. (2007). Biochar and bioenergy production for climate change mitigation. *N. Z. Sci. Rev.* **64,** 5–10.

Woolf, D., Amonette, J. E., Street-Perrott, F. A., Lehmann, J., and Joseph, S. (2010). Sustainable biochar to mitigate global climate change. *Nat. Commun.* **1**(56), 1–9.

Xu, C., Liu, W., and Sheng, G. D. (2008). Burned rice straw reduces the availability of clomazone to barnyardgrass. *Sci. Total Environ.* **392,** 284–289.

Yamamoto, M., Okimori, Y., Wibowo, I. F., Anshori, S., and Ogawa, M. (2006). Effects of the application of charred bark of *Acacia mangium* on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. *Soil Sci. Plant Nutr.* **52,** 489–495.

Yanai, Y., Toyota, K., and Okazaki, M. (2007). Effects of charcoal addition on N2O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments. *Soil Sci. Plant Nutr.* **53,** 181–188.

Yang, Y. N., and Sheng, G. Y. (2003). Enhanced pesticide sorption by soils containing particulate matter from crop residue burns. *Environ. Sci. Technol.* **37,** 3635–3639.

Yang, Y. N., Sheng, G. Y., and Huang, M. (2006). Bioavailability of diuron in soil containing wheat- straw-derived char. *Sci. Total Environ.* **354,** 170–178.

Yao, F. X., Arbestain, M. C., Virgel, S., Blanco, F., Arostegui, J., Macia-Agullo, J. A., and Macias, F. (2009). Simulated geochemical weathering of a mineral ash-rich biochar in a modified Soxhlet reactor. *Chemosphere* **80,** 724–732.

Yeardley, R. B., Lazorchak, J. M., and Gast, L. C. (1996). The potential of an earthworm avoidance test for evaluation of hazardous waste sites. *Environ. Toxicol. Chem.* **15,** 1532–1537.

Yoshida, T., and Antal, M. J. Jr. (2009). Sewage sludge carbonization for terra preta applications. *Energy Fuels* **23,** 5454–5459.

Yu, X. Y., Ying, G. G., and Kookana, R. S. (2006). Sorption and desorption behaviors of diuron in soils amended with charcoal. *J. Agric. Food Chem.* **54,** 8545–8550.

Yu, X. Y., Ying, G. G., and Kookana, R. S. (2009). Reduced plant uptake of pesticides with biochar additions to soil. *Chemosphere* **76,** 665–671.

Yu, X. Y., Pan, L. G., Ying, G. G., and Kookana, R. S. (2010). Enhanced and irreversible sorption of pesticide pyrimethanil by soil amended with biochars. *J. Environ. Sci.* **22,** 615–620.

Zhang, P., Sheng, G., Wolf, D. C., and Feng, Y. (2004). Reduced biodegradation of benzonitrile in soil containing wheat residue-derived ash. *J. Environ. Qual.* **33,** 868–872.

Zhang, P., Sheng, G. G., Feng, Y., and Miller, D. M. (2005). Role of wheat-residue-derived char in the biodegradation of benzonitrile in soil: Nutritional stimulation versus adsorptive inhibition. *Environ. Sci. Technol.* **39,** 5442–5448.

Zheng, W., Guo, M., Chow, T., Bennett, D. N., and Rajagopalan, N. (2010). Sorption properties of greenwaste biochar for two triazine pesticides. *J. Hazard. Mater.* **181,** 121–126.

CHAPTER FOUR

Phytostabilization: A Green Approach to Contaminant Containment

Nanthi S. Bolan,[*,†] Jin Hee Park,[*,†,1] Brett Robinson,[‡]
Ravi Naidu,[*,†] *and* Keun Young Huh[§]

Contents

* Centre for Environmental Risk Assessment and Remediation (CERAR), University of South Australia, Adelaide, Australia
† Cooperative Research Centre for Contaminants Assessment and Remediation of the Environment (CRC CARE), University of South Australia, Adelaide, Australia
‡ Department of Soil Science, Lincoln University, Lincoln, New Zealand
§ Department of Landscape Architecture, Gyeongnam National University of Science and Technology, Dongjin-ro 33, Jinju, Gyeongnam, Republic of Korea
1 Current address: Centre for Mined Land Rehabilitation (CMLR), University of Queensland, Brisbane, Australia

Advances in Agronomy, Volume 112
ISSN 0065-2113, DOI: 10.1016/B978-0-12-385538-1.00004-4

Abstract

Phytostabilization involves the establishment of a plant cover on the surface of the contaminated sites with the aim of reducing the mobility of contaminants within the vadose zone through accumulation by roots or immobilization within the rhizosphere, thereby reducing off-site contamination. The process includes transpiration and root growth that immobilizes contaminants by reducing leaching, controlling erosion, creating an aerobic environment in the root zone, and adding organic matter to the substrate that binds the contaminant. Microbial activity associated with the plant roots may accelerate the degradation of organic contaminants such as pesticides and hydrocarbons to nontoxic forms. Phytostabilization can be enhanced by using soil amendments that immobilize metal(loid)s combined with plant species that are tolerant of high levels of contaminants and low-fertility soils or tailings. Although this technology is effective in the containment of metal(loid)s, the site requires regular monitoring to ensure that the stabilizing conditions are maintained. Soil amendments used to enhance immobilization may need to be periodically reapplied to maintain their effectiveness. We critically examine the applicability of this technology to manage metal(loid)s contaminated soils and identify fertile areas for future research.

1. Introduction

Phytoremediation comprises technologies that use higher plants to clean up and revegetate contaminated sites (Adriano *et al.*, 2004; Pulford and Watson, 2003; Robinson *et al.*, 2009). Many techniques and applications are included in the term phytoremediation. They differ in the process by which plants can remove, immobilize, or degrade contaminants. For example, the process in which plants are used to remove organic or inorganic contaminants from soil and water and store them in harvestable tissue is called phytoextraction, rhizoextraction, or phytofiltration. Similarly, the technique in which plants are used to remove contaminants through volatilization is called phytovolatilization (Moreno *et al.*, 2005). In phytostabilization, inorganic contaminants such as heavy metal(loid)s in the soil are immobilized, thereby minimizing their transport in water or dust. This technology may enhance the degradation of organic contaminants such as pesticides and hydrocarbons via microbial activity associated with the plant roots that accelerates the transformation of these contaminants into nontoxic forms (Berti and Cunningham, 2000).

Phytostabilization aims to contain contaminants within the vadose zone through accumulation by roots or precipitation within the rhizosphere. This prevents off-site contamination through their migration via wind and water erosion, leaching, and soil dispersion. Phytostabilization also refers to



Plate 1 **Organic amendments reduce metal toxicity in mine tailings (Moreno *et al.*, 2005).**

establishing a plant cover on the surface of the contaminated soils, which reduces their exposure to wind, water, and direct contact with humans or animals. Phytostabilization can be enhanced by using soil amendments that are effective in the immobilization of metal(loid)s and plant species that are tolerant of high levels of contaminants (Plate 1; Kumpiene *et al.*, 2007; Park *et al.*, 2011a; Vangronsveld *et al.*, 1995a).

Phytostabilization reduces the mobility, and therefore the risk, of inorganic contaminants without necessarily removing them from the site. This technology does not generate contaminated secondary waste that needs further treatment. It also enhances soil fertility, thereby achieving ecosystem restoration. However, since the contaminants are left in place, the site requires regular monitoring to ensure that the optimal stabilizing conditions are maintained. If soil amendments are used to enhance immobilization, they may need to be periodically reapplied to maintain their effectiveness (Bolan *et al.*, 2003a; Keller *et al.*, 2005).

While some organic contaminants undergo microbial or chemical degradation, inorganic contaminants such as metal(loid)s are immutable. Therefore, containment of metal(loid)s through phytostabilization is critical in managing contaminated sites. This review examines the various approaches to remediate contaminated sites; processes involved in phytostabilization of metal(loid)s; soil and plant factors affecting this technology; advantages and disadvantages; and enhancement of this technology using soil amendments.

2. The Importance of Bioavailability in Phytostabilization

Naidu *et al.* (2008a) defined the bioavailability of contaminants in soil as the fraction of the total metal(loid) in the interstitial pore water (i.e., soil solution) and soil particles that is available to the receptor organism. There is controversy in the literature regarding the definition and the methods for the measurement of bioavailability. Microbiologists often regard the concentration that can induce a change either in morphology or physiology of the organism as the bioavailable fraction, whereas plant scientists regard the plant available pool as the bioavailable fraction (Adriano *et al.*, 2004). Recent studies (e.g., McLaughlin *et al.*, 2000; Peijnenburg *et al.*, 2007; Vig *et al.*, 2003) indicate that the transformation of contaminants in soils is a dynamic process, which indicates that bioavailability changes with time.

A generic definition of *bioavailability* is the potential for living organisms to take up metal(loid)s through ingestion or from the abiotic environment (i.e., external) to the extent that the metal(loid)s may become involved in the metabolism of the organism (NRC, 2003). More specifically, it refers to the biologically available fraction (or pool) that can be taken up by an organism and can react with its metabolic machinery, or it refers to the fraction of the total concentration that can interact with a biological target (Vangronsveld and Cunningham, 1998). Bioavailability requires that the metal(loid)s come in contact with the organism (i.e., physical accessibility). Moreover, metal(loid)s need to be in a particular form (i.e., chemical accessibility) to enter biota. Bioavailable metal(loid)s are soluble and in an accessible form to the target organism.

Immobilization technologies minimize the bioavailability of metal(loid)s by allowing them to react with the soil for a longer period (aging; i.e., natural attenuation) or by adding soil amendments. Many studies have documented the effect of aging on the immobilization of metal(loid)s in soils (Lock and Janssen, 2003; Lothenbach *et al.*, 1999) and also the potential value of various organic and inorganic soil amendments in reducing the bioavailability of metal(loid)s in soil (Cheng and Hseu, 2002; Kumpiene *et al.*, 2007; Park *et al.*, 2011a). For example, various phosphate compounds have been found to be effective in the immobilization of Pb in soils (McGowen *et al.*, 2001), and USEPA recommends this technique for risk-based remediation of Pb-contaminated sites (USEPA, 2001) (refer to Section 7).

3. Phytostabilization Concepts

Most legislative schemes require that a soil be remediated if the total concentration of one or more contaminants (e.g., heavy metal(loid)s) is exceeded in a designated part (topsoil, subsoil) of the soil profile (Swartjes,

1999). Such a regulatory environment is not conducive to phytostabilization, since in an ideal phytostabilization operation, the total concentration of metal(loid) contaminants remain unchanged.

Regulators are now recognizing the influence of metal(loid) solubility and mobility on environmental risk. Consequently, there is an increasing adoption of a risk-based approach when assessing soil quality (Fernandez *et al.*, 2005; Naidu *et al.*, 2008b; Swartjes, 1999). Such risk-based regulatory systems are based on the effect of the contaminant, rather than on its total concentration in the soil (Naidu *et al.*, 2008b). Higher plants immobilize metal(loid)-polluted soils by affecting changes in the rhizosphere, which has distinct physical, chemical, and biological conditions. The rhizosphere is the few millimeters of soil surrounding the plant roots and influenced by their activity as well as the microbial assemblages associated with the roots. Functionally, the rhizosphere is a highly dynamic, solar/plant-driven microenvironment that is characterized by feedback loops of interactions between root processes, soil characteristics, and the dynamics of the associated microbial population (Adriano *et al.*, 2004; McGrath *et al.*, 2001). Soil characteristics such as pH and redox potential, nutrient status, the presence of contaminants, and physical properties all influence plant growth and the dynamics of microbial population (Marschner *et al.*, 2001). Most root exudates are ultimately responsible for many of the rhizosphere's unique characteristics. Root exudates stimulate microbial activity and biochemical transformations and/or enhancement of mineralization of metal(loid)s in the rhizosphere (Anderson *et al.*, 1993; Paterson, 2003). Between 10% and 40% of the total net C assimilated by crops is released in the form of soluble root exudates and insoluble materials such as cell walls and mucilage (Bolan *et al.*, 2011; Rasse *et al.*, 2005).

The chemical and biological reactions occurring in the rhizosphere play an important role in the bioavailability of metal(loid)s to plants. Plant roots change the physical, chemical, and biological conditions of the soil in the rhizosphere which, in comparison to bulk soil, is enriched with organic substances of plant and microbial origin, including organic acids, sugars, amino acids, lipids, coumarins, flavonoids, proteins, enzymes, aliphatics, aromatics, and carbohydrates (Chang *et al.*, 2002; Hinsinger *et al.*, 2005). Common organic acids in the rhizosphere are acetic, butyric, citric, fumaric, lactic, malic, malonic, oxalic, propionic, tartaric, and succinic acids. Organic acids in the rhizosphere affect the dynamics of metal(loid)s in soils via their effect on acidification, metal(loid)s chelation and complexation, precipitation, redox reactions, microbial activity, rhizosphere physical properties, and root morphology.

Plants may be identified and/or engineered that exude compounds capable of immobilizing contaminants using redox processes or precipitation of insoluble compounds in the rhizosphere. For example, Pb is precipitated as phosphate (Cotter-Howells and Caporn, 1996; Cotter-Howells

et al., 1994) and Cd forms complexes with sulfide (de Knecht *et al.*, 1994) in the roots and the rhizosphere of *Agrostis capillaris* and *Silene vulgaris*, respectively.

Plants reduce the mobility and transport of pollutants in the environment either by uptake or immobilization (Pulford and Watson, 2003). Phytostabilization can be enhanced by using soil amendments that are effective in the immobilization of metal(loid)s and is readily suited to the monitored natural remediation of contaminated sites, which is employed within the context of a carefully controlled and monitored site cleanup strategy to be able to achieve site-specific remediation objectives within a time frame that is more reasonable than that offered by other more invasive methods (Adriano *et al.*, 2004; Fig. 1).

Volatilization of contaminants into atmosphere via plants may be an important process in the phytostabilization of soils where high concentrations of organic contaminants are present (Ouyang, 2002; Schnoor *et al.*, 1995). Phytovolatilization has some potential to remediate soils contaminated with metal(loid)s that form volatile hydride and methyl compounds. Recent efforts have concentrated on developing transgenic species with increased potential for volatilizing Hg (Moreno *et al.*, 2005; Rugh *et al.*, 1998) and Se (de Souza *et al.*, 2002; Robinson *et al.*, 2009; Terry *et al.*, 2000). One drawback of volatilization is that there is no control on the final destination of the contaminants.

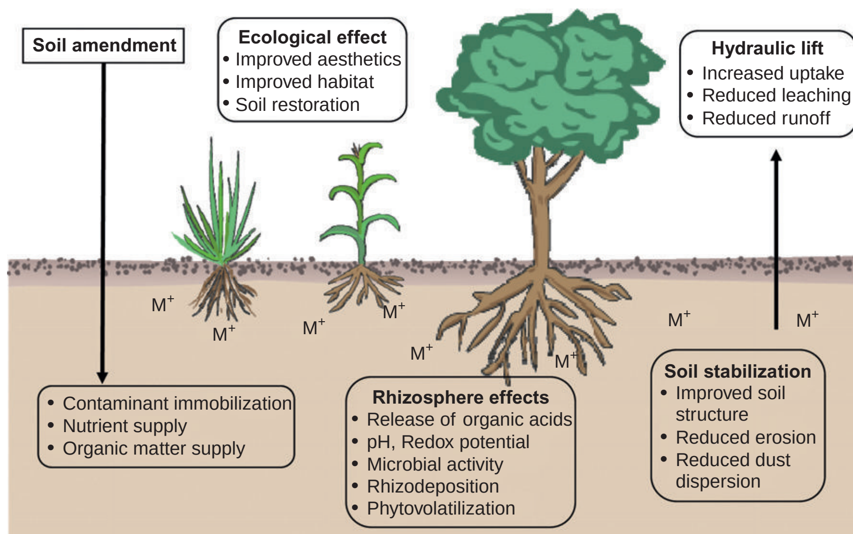


Figure 1 Schematic diagram illustrating the potential action of phytostabilization on contaminants in soil.

4. Processes Involved in Phytostabilization

Figure 2 shows the processes involved in reducing the mobility and bioavailability of contaminants. The most important of these are

- uptake and sequestration of contaminants in the root system;
- alteration of soil factors that influence the speciation and immobilization of contaminants (pH, organic matter, redox levels);
- root exudates that regulate the precipitation and immobilization of the contaminants;
- establishment of vegetation barrier that reduces the likelihood of physical contact with the soil by animals and humans;
- mechanical stabilization of the site to minimize erosion by wind and water;
- enhancement of evapotranspiration, thereby reducing the leaching of contaminants.

4.1. Contaminant removal

Although the removal of contaminants through plant uptake may not be the main process involved in phytostabilization, plant removal of contaminants may still play a role in this technology. Fässler *et al.* (2010) showed that

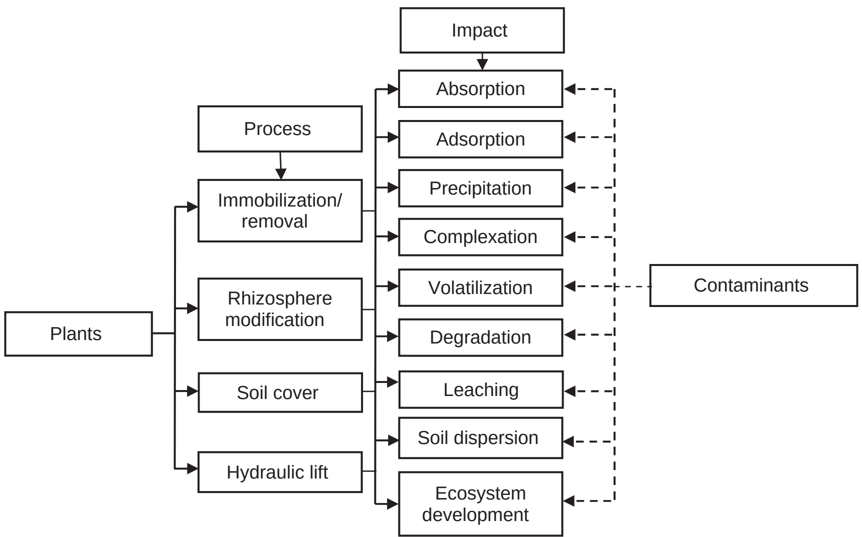


Figure 2 Processes involved in the phytostabilization of contaminants.

agricultural crops could enhance the phytostabilization of a metal-contaminated soil, while producing Zn-rich biomass that could be used as nutritious stock fodder. Poplars used in the phytostabilization of a B-contaminated sawdust pile extracted high concentrations of B (Robinson *et al.*, 2007). Here the biomass could be used as a B-rich mulch on nearby orchards that were deficient in this element. In both cases, the primary role of the plants was the stabilization of the site. The extraction of the metal(loid)s enhanced the value of the biomass.

Hyperaccumulating plants that are effective in the removal of metal(loid)s can be used to enhance this technology (Wong, 2003). Plants employ various mechanisms to take up metal(loid)s from soil (Table 1). For example, concentrations of phytosiderophores up to molar levels have been measured for nonsterile conditions in the rhizosphere of Fe-deficient plants (Romheld, 1991). Awad *et al.* (1994) found enhanced Fe mobilization up to a distance of 4 mm from the wheat roots and concluded that phytosiderophores are highly effective in Fe acquisition. Phytosiderophores also form chelates with Zn, Cu, and Mn and facilitate the solubilization of these metals in calcareous soils (Romheld, 1991; Shenker *et al.*, 2001). Grasses release phytosiderophores in response to Zn deficiency (Cakmak *et al.*, 1994; Walter *et al.*, 1994; Zhang *et al.*, 1991). Cakmak *et al.* (1996) demonstrated that the enhanced release of phytosiderophores correlates with Zn efficiency in wheat genotypes. Von Wiren *et al.* (1996) proposed two possible pathways for the uptake of Zn from Zn phytosiderophores in grasses: (1) via the transport of the free Zn cation and (2) the uptake of nondissociated Zn–phytosiderophore complexes. A defining feature of these metal(loid) transport systems is that they have poor specificity (Reid and Hayes, 2003). Therefore, nonessential metal(loid) ions with a similar size to nutrients may be taken up into the symplast and ultimately be translocated to the shoots. Khattak *et al.* (1991) and Peryea and Kammereck (1997) demonstrated that plants take up arsenate (AsO_4^{3-}) via the same physiological mechanism as phosphate (PO_4^{3-}). Similarly, Tl^+ may enter via the K^+ ion channel (Skulsky, 1991), Cd^{2+} may enter via either Ca^{2+} or Zn^{2+} transport system, and Ni^{2+} may enter along with Mg^{2+}.

Mench and Martin (1991) collected dissolved root exudates from two tobacco species (*Nicotiana tabacum*, *Nicotiana rustica*) and corn (*Zea mays*) to extract metal(loid)s from two soils. They observed increased extractability of Mn and Cu, while Ni and Zn remained recalcitrant. Root exudates from the tobacco species enhanced the solubility of Cd, and the amount extracted by the root exudates was in the range of Cd uptake in these plants grown on soil (*N. tabacum* > *N. rustica* > *Z. mays*). Therefore, increased solubility of Cd in the rhizosphere due to the release of organic exudates in the apical root zone can be viewed as a mechanism promoting Cd accumulation in tobacco.

Youssef and Chino (1989) found relatively lower concentrations of dissolved Cu and Zn in the rhizosphere soil being associated with higher pH.

Table 1 Selected references on the plant-based processes involved in the containment of contaminants

Contaminant	Substrate	Plant species	Containment process	Reference
Hg	Base metal tailings	*Brassica juncea*	Phytovolatilization and phytoextraction	Moreno *et al.* (2005)
Cr(VI)	Mineral soil	*Brassica juncea*	Reduction	Bolan *et al.* (2003b)
Cd	Variable charge soil	*Brassica juncea*	Phytoimmobilization	Bolan *et al.* (2003c)
Cu	Soil	*Brassica napus* L.	Chelation followed by uptake	Zeremski-Škoric *et al.* (2010)
Cu	Pasture soil	*Agrostis tenuis*	Chelation followed by uptake but resulted in Cu leaching	Thayalakumaran *et al.* (2003)
Pb	Hydroponics media	Alfalfa (*Medicago sativa*)	Chelation followed by uptake	López *et al.* (2005)
As	Orchard soil	Pome fruit trees	Phosphate-induced desorption followed by plant uptake	Peryea (1991)
As	Tailings	*Brassica Juncea*	Phytoextraction	Ko *et al.* (2008)
Mo			Phosphate-induced desorption followed by plant uptake	Neunhauserer *et al.* (2001)
Cd, Cr, Cu, Ni, Pb, Zn	Multimetal-contaminated soil	Canola (*Brassica napus*) and radish (*Raphanus sativus*)	Phytoextraction	Marchiol *et al.* (2004)
Pb, Cd, Cu	Artificially contaminated with 600 mg kg^{-1} Pb, 40 mg kg^{-1} Cd, and 100 mg kg^{-1} Cu	*Echinochloa crus-galli*	Root exudates-enhanced phytoextraction	Kim *et al.* (2010)
Cd, Cu, Pb, Zn	Mining soil	*Sedum alfredii*	Chelation followed by uptake	Liu *et al.* (2008)
Cd, Cu, Ni, Pb, Zn	Calcareous dredged sediment derived surface soil	*Brassic rapa*, *Cannabis sativa*, *Helianthus annuus*, *Zea mays*	Chelation followed by uptake	Meers *et al.* (2005)
Cd, Cr, Cu, Pb, and Zn	Multiply metal-contaminated soil,	*Brassica Juncea*	Chelation followed by uptake	Quartacci *et al.* (2006)

(*Continued*)

Table 1 (*Continued*)

Contaminant	Substrate	Plant species	Containment process	Reference
Pb	Artificially polluted by 800 mg Pb $(NO_3)_2$.	Maize (*Zea mays* L.)	Improved metal uptake by plant growth regulators (GA_3 and IAA) and EDTA	Hadi *et al.* (2010)
Cu, Pb, Zn	Paddy soils contaminated by several toxic metals under aerobic soil conditions	Rice (*Oryza sativa* L.), soybean (*Glycine max* [L.] Merr.), and maize (*Zea mays* L.)	Phytoextraction	Murakami and Ae (2009)
Cd	Unpolluted surface layer farmland soil spiked with Cd	*Solanum nigrum* L.	Improved plant growth and Cd uptake by fungi and citric acid	Gao *et al.* (2010)
U, Cd, Cr, Cu, Pb, Zn	Ra production site contaminated with Ra, U, and heavy metals	Mustard (*Brassica juncea*), ryegrass (*Lolium perenne*)	Chelation followed by uptake	Duqučne *et al.* (2009)
Hg	Tailings dam of the abandoned metal mine	*Brassica juncea*	Phytoextraction followed by phytovolatilization	Moreno *et al.* (2005)
Hg	Soil	Transgenic tobacco	Phytovolatilization	He *et al.* (2001)
Se	Se added soil	*Lycopersicon esculentum, Brassica oleracae, Festuca arundinacae, Medicago sativa, Astragalus bisulcatus*	Phytovolatilization	Duckart *et al.* (1992)
Se	Soil amended with dimethylselenoniopropionate, selenomethionine, sodium selenite, or sodium selenate	Indian mustard (*Brassica juncea* L.)	Phytovolatilization	de Souza *et al.* (2000)

Neng-Chang and Huai-Man (1992) observed that the impact of root activity on the rhizosphere pH was influenced by edaphic conditions. For example, the extractability of Cd by 0.1 M $CaCl_2$ was inversely correlated with the pH. In turn, the uptake balance between the anions and the cations influenced the rhizosphere pH. Thus, in terms of physiologically controlled mechanism, uptake of nitrate from fertilizer application could induce higher rhizosphere pH, limiting the solubilization of metals and their subsequent uptake. Whereas an increase in soil pH can increase the concentration of mobile metal(loid) species such as As^{5+} and Cr^{6+} and also increase the solubilization of organic matter, thereby releasing metal(loid)s that are associated with organic matter (Bolan *et al*., 2011; van Herreweghe *et al*., 2002).

The establishment of mycorrhizal fungi is a prerequisite for the success of any soil restoration program (Haselwandter and Bowen, 1996; Meier *et al*., 2011), and hence the relationships between roots and microorganisms in the rhizosphere need to be elucidated. Inoculation with specific mycorrhizal fungi has been considered to increase the uptake of nutrients and pollutants by phytoextractor species (Entry *et al*., 1996). Rogers and Williams (1986) found that inoculation of *Melilotus officinalis* and *Sorghum sudanense* with vesicular arbuscular mycorrhizae increased the uptake of ^{137}Cs by 30 Bq g^{-1} ash. The association of *Pteris vittata* with mycorrhizal fungi increased its capacity to uptake As up to 1031 mg As kg^{-1} dry weight compared to 527 mg As kg^{-1} in the nonmycorrhizal plants (Leung *et al*., 2010). Similarly, Díaz *et al*. (1996) reported increased mycorrhizal fungi enhanced plant metal tolerance (Schutzendubel and Polle, 2002) by absorbing metal(loid)s in their hyphal sheath and external mycelium. The hydrophobic fungal sheath may reduce metal(loid) access to the root. Fungal chelants may complex metal(loid)s reducing their bioavailability (Jentschke and Godbold, 2000). The mechanisms of plant nutrient uptake by the fungi and their subsequent translocation into the root may be more specific than the corresponding plant uptake mechanisms, reducing the amount of toxic metal(loid)s that enter the plant (Meier *et al*., 2011).

Results from greenhouse studies on the effect of mycorrhizae on contaminant uptake cannot be directly extrapolated to field conditions because of varying environmental conditions and time scale (short-term green house vs. long-term field conditions). Plant physiological and soil conditions in the field typically differ greatly, both spatially and temporally from those obtained in greenhouse experiments (Entry *et al*., 1996).

4.2. Soil cover

Vegetation acts as a sink for contaminants by uptake or assimilation, thus reducing the amount of contaminant available for transport to groundwater. Vegetative cover also plays a vital role in stabilization by reducing the water flux through the soil profile and mechanically stabilizing the soil through

root growth. This reduces the movement of soil and the associated contaminants. Soil erosion potential is increased if the soil has no or sparse vegetative cover of plants and/or plant residues. Plant and residue cover protects the soil from rain-splash and slows the movement of surface runoff thereby increasing infiltration. Similarly, vegetation reduces the wind velocity, thereby mitigating the dispersion of soil and sediments. The vegetation-induced reduction in soil erosion is likely to reduce the movement of contaminants and subsequent off-site contamination (Table 2).

The major effects of vegetation on water and wind erosion include:

- interception of the direct impact of rainfall drops and wind;
- decreasing the velocity of runoff, and hence the cutting action of water and its capacity to entrain soil and sediment;
- root-induced compaction and increases in soil strength, aggregation, and porosity;
- enhancement of vegetation-induced biological activities and their influence on soil aggregation and porosity;
- transpiration of water, leading to the subsequent drying out of the soil;
- insulation of the soil against temperature variation which can result in cracking or "frost heave."

The erosion-reducing effectiveness of plant and/or residue covers depends on the type, extent, and quantity of cover (Fig. 3). Vegetation and residue combinations that completely cover the soil, and which intercept all falling raindrops at and close to the surface, are the most efficient in controlling soil erosion. Residual roots and earthworms are also important as these provide channels (biopores) that allow surface water to move into the soil, thereby reducing surface runoff and soil erosion (Bronick and Lal, 2005; McCallum *et al.*, 2004). Maintaining living ground covers, to provide the best protection against loss of soil because they slow down runoff water after rain, allows water to infiltrate into the soil and lessen evaporation losses. For example, vegetative cover in rehabilitated mined land increased infiltration rate and declined erosion from stimulated storm from 30–35 t ha^{-1} at 0% vegetative cover to 0.5 t ha^{-1} at 47% cover (Loch, 2000). Tree roots were found to increase soil strength by 2–8 kPa depending on species, while grass roots contributed 6–18 kPa, thereby decreasing the erosion potential of soils (Simon and Collison, 2002).

Lumber production is an important land use in New Zealand. Plantation forests of *Pinus radiata* cover some 6% of the land area. To prevent decay, lumber products are treated with biocides, with Copper Chromium and Arsenic (CCA) being the treatment of choice. Historically, pentachlorophenol (PCP) has been used. Boron is used to prevent sap stain. The use of these treatments has resulted in the contamination of sites used for wood waste disposal. Piles of wood waste, primarily sawdust, leach B, CCA, and PCP thus pose a serious environmental risk. One such pile, 3.6 ha and

Table 2 Selected references on the value of vegetative cover in reducing dust dispersion and erosion control

Plant species	Soil	Observations	Reference
Honey mesquite (*P. glandulosa*)	Semiarid area	Vegetative cover reduces wind erosion.	Hupy (2004)
Spontaneous plant communities *Piptatherum miliaceum Dittrichia viscosa*, *Helichrysum decumbens*, *Phagnalon saxatile*, *Sonchus tenerrimus*	Tailings	Plant communities reduce air borne and water erosion and may mitigate the spread of the contamination to the nearby areas.	Conesa *et al.* (2007)
Neyrudia reyaudinana, Imperta cylindraca, Rhus chinensis, and *Pteridium aquilium*	Lead/Zinc mine	Vegetation in mine tailings and disposal sites of dredged material will reduce erosion by water and wind.	Lan *et al.* (1997)
Smooth brome (*Bromus inermis* Leyss.) Red fescue (*Festuca rubra* L.) Perennial ryegrass (*Lolium perenne* L.) Alfalfa (*Medicago sativa* L.) Buckwheat (*Fagopyrum esculentum* Moench)	Coarse taconite iron ore tailing	Vegetative cover has improved depending on the type of municipal solid waste compost used and rate of application. Overall plant cover across all treatments has improved from zero prior to experimental manipulation to 83% after 4 years.	*Norland and Veith (1995)*
Lygeum spartum and *Piptatherum miliaceum, Cicer arietinum* (chickpea)	Mine tailings	Stabilization of the tailings using vegetation or other means would reduce both wind and water erosion.	Conesa *et al.* (2009)
Pioneer birch trees	The historical hard coal mining area-dumps	Vegetation on a dump surface protects from erosion and reduces the seepage water formation by evapotranspiration.	Willscher *et al.* (2010)
Rhodes grass (*Chloris gayana*) kikuyu (*Pennisetum clandestinum*)	Mine site	Erosion from the simulated storm was greatly reduced by vegetative cover, declining from 30–35 t ha^{-1} at 0% vegetative cover to 0.5 t ha^{-1} at 47% cover.	Loch (2000)

(*Continued*)

Table 2 (*Continued*)

Plant species	Soil	Observations	Reference
Rosmarinus officinalis, *Triticum aestivum,* natural-spontaneous vegetation	Hill slopes	The vegetative covers of *Rosmarinus officinalis* and natural-spontaneous vegetation reduced the soil losses by 99% and 98%, with respect to the *Triticum aestivum*, and the runoff losses by 94% and 96%, respectively. Also, the *Rosmarinus officinalis* and natural-spontaneous plants influenced infiltration by intercepting much of the rainfall water respect to the *Triticum aestivum*.	Zuazo *et al.* (2004)
Huisache (*Acacia* sp.), Mesquite (*Prosopis* sp.), Prickly Pear, or Nopal (*Opuntia* sp.), Cardon (*Opuntia imbricata*)	Semiarid area	Runoff was reduced by 87%, 87%, and 98% and soil loss by 97%, 93%, and 99% for *Acacia farnesiana*, *Prosopis laevigata*, and *Opuntia* sp., respectively, as compared to the Control.	Vásquez-Méndez *et al.* (2010)

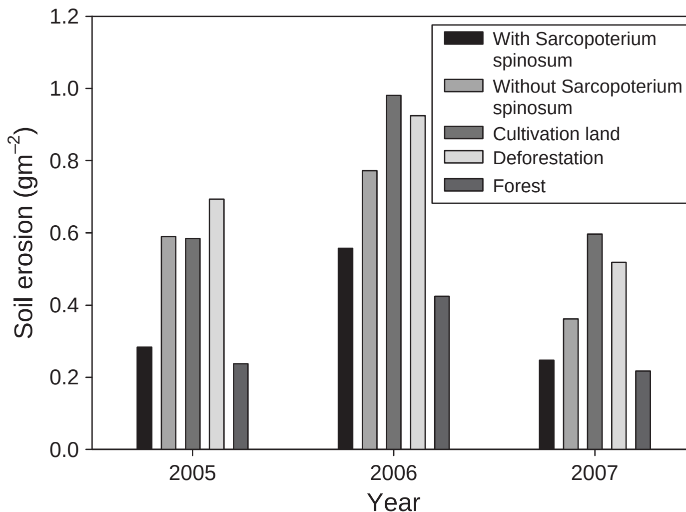


Figure 3 Total soil erosion (g m^{-2}) in different soil treatments: natural vegetation dominated by *Sarcopoterium spinosum;* natural vegetation where the *S. spinosum* was removed repeatedly; cultivation practices wherein all vegetative cover was removed and cleared; deforestation areas (cutting has been practiced on *Pinus halepensis* over the last 20 years); afforestation (*Pinus halepensis)* planted in 1960 (Mohammad and Adam, 2010).

located near the town of Kopu, New Zealand, was leaching high concentrations of B into local streams, resulting the degradation of ecosystems and fisheries. The presence of high B concentrations and a C:N ratio of 400 had prevented vegetation from establishing on the pile. Consequently, virtually all of the annual 1135 mm of rainfall resulted in leaching events. Saturated material occurred at depths as shallow as 20 mm, resulting in anaerobic conditions that reduced the rate of biodegradation of the wood waste and resulted in methane production.

Robinson *et al.* (2007) describes the phytostabilization of this pile using poplar trees. Poplar clones were selected that tolerate high B concentrations (Plate 2). The pile was heavily fertilized with nitrogen, and a collection pond to store any leachate was installed at the foot of the pile. After 3 years of growth, the trees have reduced leaching events from the pile during the Southern hemisphere winter (June–September). The holding pond collects most of this leachate, which is used for irrigation during the summer months. Occasional winter storms result in the holding pond discharging into the local stream. However, these storm events result in dilution of the contaminants to levels below the New Zealand Drinking Water Standard of 1.4 mg L^{-1}B.



Plate 2 Phytostabilization of timber treatment site in Kopu, New Zealand (Robinson *et al.*, 2007).

The poplar trees accumulated high concentrations (>1000 mg kg^{-1}) of B in the leaves, while the concentrations of other contaminants, namely Cu, Cr, and As, were all <1 mg kg^{-1}. It was suggested that the trees be periodically coppiced and used as an organic B-rich mulch on nearby orchards that are deficient in this essential micronutrient. Such a strategy relies on only coppicing a fraction of the trees on the pile, so that hydraulic control is maintained.

4.3. Rhizosphere modification

Rhizosphere-induced changes in soil biochemical properties regulate the transformation, mobility, and bioavailability of metal(loid)s, thereby affecting the phytostabilization of contaminated sites. The major rhizosphere-induced biochemical properties that influence metal(loid) dynamics include acidification, release of organic acids, and increased microbial activity (Table 3).

Table 3 Selected references on processes involved in rhizosphere modification

Plant species	Substrate	Rhizosphere modification	Reference
Camellia japonica	Pasture soil	Decrease in pH, resulting in the dissolution of rock phosphate	Zoysa *et al.* (1997)
Clover	Pasture soil	Decrease in pH, resulting in the dissolution of rock phosphate	Bolan *et al.* (1996)
Brassica carinata	Metal-contaminated soil mixed with peat	Mobilization of metals in the rhizosphere by its acidification and complexation with organic acids present in root exudates	Quartacci *et al.* (2009)
Lupinus albus L.	Heavy metal-contaminated soil	Increase in water-soluble carbon and redox potential, resulting in the reduction of bioavailability, increase microbial activity	Martínez-Alcalá *et al.* (2010)
Thlaspi goesingense	Soil from serpentine site	Increase in DOC and water-soluble Ni concentrations	Wenzel *et al.* (2003)
Pteris vittata	As contaminated soil	Increase in DOC and pH, resulting in the increase in water-soluble As	Gonzaga *et al.* (2006)
Lolium perenne L.	Zn-contaminated soil	Increase in low-molecular-weight organic acids and amino acids, resulting in the increased available Zn fraction	Xu *et al.* (2007)
Thlaspi caerulescens	Agricultural topsoil where wastes from septic tanks had been applied regularly	Increase in DOC, resulting in the mobilization and complexation of Zn and Cd	Dessureault-Rompré *et al.* (2010)
Betula papyrifera	Contaminated soil from a Cu–Ni smelter	Decrease in pH and increase in DOC, resulting in the water and $BaCl_2$ extractable metal concentration	Legrand *et al.* (2005)

The major source of plant-based OH^{-}/H^{+} fluxes affecting pH in the rhizosphere is related to the differential uptake of cations and anions by plant roots (Tang and Rengel, 2003). For example, plants receiving NH_4^{+} will counterbalance the corresponding excess of positive charges by releasing equivalent amounts of H^{+} in the rhizosphere, thereby decreasing rhizosphere pH. Apart from this, nitrogen transformation and nitrate leaching in the nitrogen cycle have been suggested to be major causes of soil acidification (Bolan and Hedley, 2003).

Acidification affects the solubility and speciation of metal(loid) ions in several ways, foremost of which include: (a) modification of surface charge in variable charge soils; (b) altering the speciation of metal(loid)s; and (c) influencing the redox reactions of the metal(loid)s (Adriano, 2001). Adsorption of metals almost invariably decreases with increasing soil acidity (or decreasing pH; Tiller, 1989; Yang *et al*., 2006). Three possible reasons have been advanced for this phenomenon (Naidu *et al*., 1994). First, in variable charge soils, a decrease in pH causes a decrease in surface negative charge resulting in lower cation adsorption. Second, a decrease in soil pH is likely to decrease hydroxy species of metal cations (MOH^{n+}) which are adsorbed preferentially over mere metal cation. And third, acidification causes the dissolution of metal(loid) compounds, resulting in an increase in their concentration in soil solution.

In the case of metalloids, such as As, the effect of soil acidity on adsorption is manifested through two interacting factors—the increasing negative surface potential on the plane of adsorption and the increasing amount of negatively charged As^{5+} species present in soil solution. While the first factor results in lower As^{5+} adsorption, the second factor is likely to increase adsorption. Thus, the pH effect on As^{5+} adsorption is largely influenced by the nature of the mineral surface. For example, in soils with low oxide content, increasing pH had little effect on adsorption, while in highly oxidic soils, adsorption decreased with increasing pH (Smith *et al*., 1999).

Carbon compounds and nutrients are released by plant roots into the rhizosphere by "rhizodeposition" (Grayston *et al*., 1997; Jones *et al*., 2004). Rhizodeposits, which mostly consist of carbohydrates, carboxylic acids, and amino acids, are responsible for enhanced microbial growth (Aira *et al*., 2010; Lynch and Whipps, 1990). The role of various compounds in root exudates has been examined for their potential impact on the biogeochemistry of metal(loid)s via complexation and redox reactions. Among the range of carboxylates exuded in the rhizosphere, malate, citrate, and oxalate are expected to have the most dramatic effect due to their implication in the complexation of metal(loid)s (Bolan *et al*., 1996; Hinsinger, 2001).

In rhizosphere, some prokaryotic (bacteria, Archaea) and eukaryotic (algae, fungi) microorganisms excrete extracellular polymeric substances (EPS), such as polysaccharides, glycoprotein, lipopolysaccharide, soluble

peptide, etc. These substances possess a substantial quantity of anion functional groups that can absorb metal(loid) ions. A number of microbes are involved in EPS production viz, *Bacillus megaterium, Acinetobacter*, *Pseudomonas aeruginosa*, sulfate-reducing bacteria, and Cyanobacteria (Satpute *et al.*, 2010). The cell wall of microbes also plays a major role in metal(loid) adsorption and redox reactions. The metal(loid)s uptake by stoichiometric interaction between functional groups of cell wall composition, including phosphate, carboxyl, amine as well as phosphodiester, has been well documented (Liu *et al.*, 2003; Schiewer and Volesky, 1995). Similarly, the higher rates of volatile Se produced from the vegetated plots with added methionine compared to bare irrigated plots have been attributed to additional microbial activity associated with plant roots (Banuelos and Lin, 2007).

4.4. Hydraulic control

Hydraulic control is the term given to the use of plants to control the migration of subsurface water through the rapid uptake of large volumes of water by the plants through transpiration. The plants are effectively acting as natural hydraulic pumps, which—when a dense root network has been established near the water table in the soil—can transpire large volume of water per day (e.g., 6 L of water plant^{-1} m^{-2} d^{-1}; equal to 2190 mm per year—Ashwath and Venkatraman, 2010). Terrestrial plants add 32 × 10^3 billion tones of water vapor to the atmosphere annually through transpiration—equivalent to about 30% of the precipitation that falls on land (Hetherington and Woodward, 2003). This fact has been utilized to decrease the migration of contaminants from surface water into the groundwater and drinking water supplies.

Plants regulate the movement of contaminants through leaching and surface runoff by controlling the flow of water in soils (i.e., hydraulic control). For example, phytostabilization (i.e., phytocapping) of contaminated sites involves placing a layer of soil material and growing dense vegetation on top of the soil layer (Chen *et al.*, 2007; Venkatraman and Ashwath, 2007). The water holding capacity of the soil layer allows it to act as a "sponge" to reduce infiltration during rain events, particularly when plants are inactive. During the growing season, the evapotranspiration activity of the plants and soil surface acts as a "bio-pump" that reduces the moisture content of the soil layer during rain and irrigation events. For an effective site water balance, it is important that appropriate plant species are chosen and the soil growing conditions including depth and fertility optimized. Trapping and consuming water in the root zone result in less volume of water to act as a vehicle to carry contaminants beyond the grasp of roots, thereby leading in their leaching to groundwater (Clothier and Green, 1997). Barton *et al.* (2005) noticed that phytostabilization of a landfill site containing coal waste using loblolly (*Pinus taeda*) and Virginia (*Pinus*

virginiana) has resulted in a decrease in the drainage volume by facilitating water loss through transpiration.

Contaminants move in soils by diffusion and mass flow processes (Grifoll and Cohen, 1996). Solutes diffuse through soils and aquifer materials in response to differences in energy from one point to another. These energy gradients may be caused by differences in concentration or temperature within the system. The principal process of movement of contaminants in soils and groundwater is mass flow. Dissolved constituents in water move through the soil, with the water acting as a carrier of the contaminants. Plant-induced hydraulic control influences both these transport processes, thereby regulating the movement of contaminants in soils (Robinson *et al.*, 2006).

Some of the metal(loid)s are essential for both microorganisms and higher plants and their physiological uptake involves both active and passive processes (Huang, 2004). Both microorganisms and higher plants exhibit specific mechanisms for the uptake of metal(loid)s that involve carrier systems associated with active ionic influxes across the cell membrane. Metabolically active processes are slower than passive absorption, demanding the presence of suitable energy source and ambient conditions. It has often been observed that an increase in transpiration rate results in higher metal(loid)s uptake, especially those elements that are taken up via passive process (Tables 4 and 5). For example, Liao *et al* (2006) and Grifferty and Barrington (2000) observed an increase in Pb and Zn uptake by lettuce and wheat, respectively, with an increase in transpiration rate. In these studies, high-transpiration rate produced significantly larger quantity of transpiration stream of water to drive water-soluble Zn and Pb uptake across plasma membranes in roots than low transpiration did (Fig. 4A and B).

5. Factors Affecting Phytostabilization

Soil, plant, contaminant, and environmental factors determine the successful outcome of phytostabilization technology in relation to both the remediation and revegetation of contaminated sites.

5.1. Soil factors

As the establishment of vegetation is critical to phytostabilization, the physical, chemical, and biological properties of soils which control plant growth determine the successful outcome of this technology. Further, soil properties also regulate the dynamics of metal(loid)s thereby affecting their stabilization in soils.

Table 4 Selected references on the effect of transpiration on the uptake of metal(loid)s

Plant species	Metal(loid)s	Observations	Reference
Lettuce	Pb: $Pb(NO_3)_2$ solutions of different concentrations (100, 200, and 300 mg L^{-1} of Pb) were added to the quartz sand.	Pb uptake by lettuce increased with an increase in transpiration rate.	Liao *et al.* (2006)
Wheat	Zn: Pots were irrigated using a fertilized solution with five different levels of: 0, 2, 10, 25, and 50 mg L^{-1}.	Zn uptake increased with an increase in transpiration rate.	Grifferty and Barrington (2000)
Wheat	Zn, Cd: Two types of sands with a low and high fertility with solutions containing various levels of Cd/Zn (0/0, 0.01/0, 0.10/0, 0.50/0, 0/25, 0.01/25, 0.10/25, 0.50/25, and 0.50/50 mg L^{-1}).	Shoot Zn and Cd levels of wheat plant increased with higher transpiration rates.	Salah and Barrington (2006)
Buckwheat (*Fagopyrum esculentum* L.)	Zn, Cu: Pots received irrigation treatments containing Zn (0 and 25 mg L^{-1}) and Cu (0, 5, 10, and 15 mg L^{-1}).	Plant Cu and Zn uptake increased with transpiration rates.	Tani and Barrington (2005)
Phytolacca americana	Cd: Zn and Mn smelter and Cu mine tailing.	There was a significantly positive relationship between the shoot Cd concentration and the leaf transpiration of *P. americana*.	Liu *et al.* (2010)
Sedum alfredii	Cd: Contaminated soil due to mining activities.	Inhibition of transpiration rate in the hyperaccumulating ecotype of *S. Alfredii* has no essential effect on Cd accumulation in shoots of the plants.	Lu *et al.* (2009)
Atriplex halimus subsp. *schweinfurthii*	Cd: Modified Hoagland nutrient solution containing cadmium chloride ($CdCl_2$; 0, 50, 100, 200, and 400 μM).	Increased $CdCl_2$ decreased chlorophyll concentration, transpiration, and root hydraulic conductivity.	Nedjimi and Daoud (2009)
Wheat seedlings (*Triticum durum*)	Cd: Hoagland–Arnon nutrient solution containing 0.04 mM of cadmium acetate.	Cadmium treatment led to an inhibition of growth rate, transpiration, and ion uptake by wheat seedlings.	Veselov *et al.* (2003)

Table 5 Selected references on using plants for hydraulic control

Plant species	Transpiration rate	Attributes for phytostabilization application	Reference
Buckwheat	The change in volumetric water content in the presence of plant was smaller than that of the control with rainfall.	The total amount of Pb in the leachate was strongly correlated with the amount of leachate. During the cultivation period, the total amount of Pb leached in the control was 1.28 mg per container, while in the presence of buckwheat, the total amount of Pb was ~22.7% of the control. Moreover, with buckwheat cultivation, Pb polluted leachate resulting from rainwater was prevented.	Honda *et al.* (2007)
Willow	Average amplitude in the 6-year-old willow cover system was 9.2 mm d^{-1} (1.5–16.9 mm d^{-1}) and amplitudes in other treatments (systems) ranged from 1.8 to 2.8 mm d^{-1}.	Phytoremediation effectiveness in establishing hydraulic control was tested using a sine wave function to describe diurnal, plant-mediated max–min water table amplitudes.	Kline (2008)
Tectona grandis	The reforested land has the highest steady infiltration rate due to better soil structure and more macropores created by root activity and high organic matter content. The soil water retention was highest in the reforested soil.	Increased infiltration and water retention will decrease surface run off and conserve soil and water, restoring the hydrological balance.	Mapa (1995)
Willow tree (*Salix* spp.)	200 L d^{-1}	Plants having these characteristics may provide an inexpensive alternative to mechanical pump and treat systems for contaminated ground water in shallow aquifers.	Gatliff (1994)

Grass and forest cover	With a continuous and invariant input of ^{90}Sr to the soil (37 kBq m^{-2} $year^{-1}$), both the predicted annual and cumulative hydrologic flux of ^{90}Sr from the soil were reduced by 16% under forest cover, relative to losses under grass cover, due to greater evapotranspiration by the forest. Mean leaching losses were 67 cm under the forest cover and 86 cm under the grass cover due to modeled differences in evapotranspiration.	Over a period of 30 years, and under various management strategies, the model predicted that $<15\%$ of the ^{90}Sr initially present in soil at a contaminated site was lost through hydrologic transport and $<53\%$ was lost by radioactive decay. Phytostabilization may be important in the management of radioactive land.	Garten (1999)
Willow (*Salix viminalis*)	Perennial root system of *Salix viminalis* lowers the risk of leaching.	Concentrations of P, K, Ca, Mg, S, Mn, Zn, Cu, Ni, and Cd increased significantly with height, which was assumed to be mainly a consequence of increasing bark proportions.	Sander and Ericsson (1998)

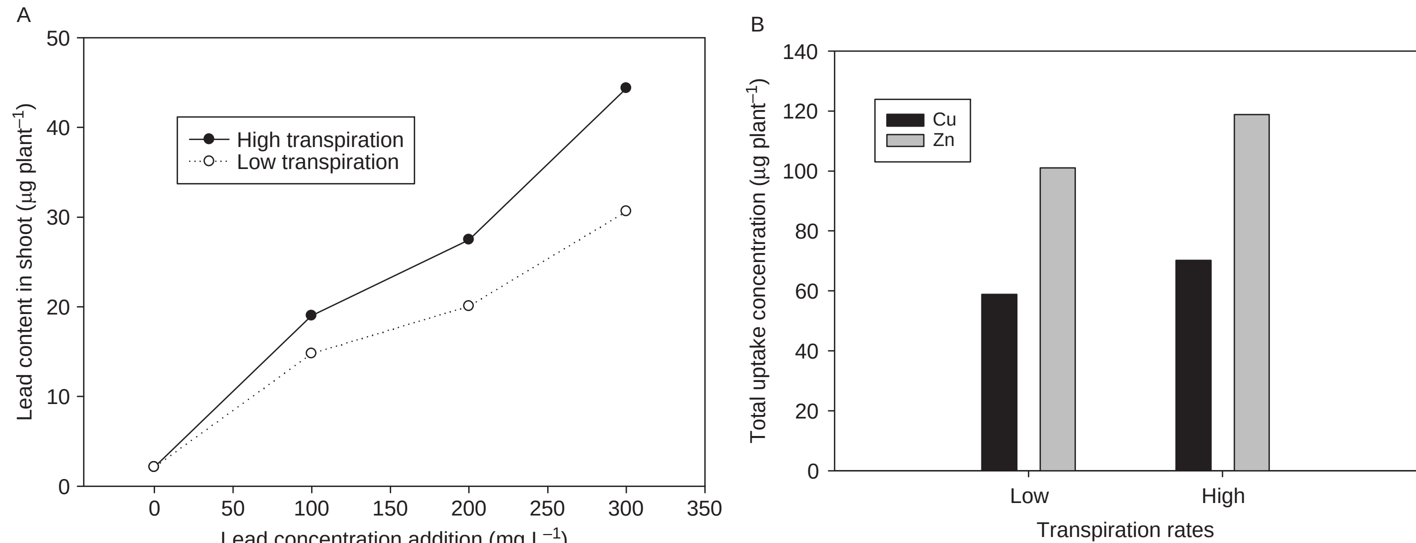


Figure 4 (A) Effect of transpiration on Pb uptake by lettuce (Liao *et al.*, 2006). (B) The mass of Cu and Zn extracted by buckwheat under low- and high-transpiration rates (Tani and Barrington, 2005).

Often, contaminated sites are not conducive for plant growth due to metal(loid) toxicity, lack of nutrients and microbial activity, and poor physical properties. For this reason, the phytostabilization of contaminated sites may require the amendment of the soils to stimulate plant growth. Some of the common amendments used to improve the soil conditions include biosolids, lime, and green waste. Some of these amendments used for improving the soil properties also enhance the efficiency of phytostabilization by altering the solubility and bioavailability of contaminants (see Section 7). For example, biosolids are generally applied to the cultivated land, given that it contains a wide range of nutrients and carbon, thereby improving the soil conditions for crop production. However, it has been recognized that the long-term application of biosolids to cultivated land has potential detrimental effect in terms of food safety due to the contaminants such as heavy metal(loid)s contained in the biosolids. Therefore, the application of biosolids to contaminated sites for phytostabilization performance will be more socially acceptable. Moreover, the contaminants in the biosolids could be also remediated by the plants.

Soil plays a significant role in controlling the immobilization and bioavailability of contaminants in the environment, thereby affecting the phytostabilization of contaminated sites. The primary soil factors influencing the immobilization and bioavailability of contaminants include soil pH, soil organic matter, cation and anion exchange capacities (AECs; available charged sites on soil surfaces), texture (clay content), and soil type.

Soil pH is one of the key parameters influencing the sorption of both inorganic and ionizable organic contaminants given that it controls virtually all aspects of contaminant and biogeochemical processes in soils. These processes include solubility, precipitation, speciation, and sorption as well as microbial activity. In most variable charge soils such as the strongly weathered tropical soils and less-weathered Andisols, increasing soil pH results in an increase in the number of negatively charged sites with a concomitant decrease in the positively charged sites (Auxtero *et al.*, 2004; Bolan *et al.*, 1999; Naidu *et al.*, 1994, 1996). In addition to its effect on surface chemical properties, soil pH also controls the speciation of contaminants. For metals, the net charge of the metal complexes and their precipitation/dissolution reactions are directly impacted by soil pH (Zeng *et al.*, 2010).

Organic contaminants and most metal(loid)s bind strongly to organic matter in soils, thereby reducing their bioavailability. Organic contaminants preferentially partition to the nonpolar domain of organic matter relative to the polar aqueous phase (Chiou *et al.*, 1984; Poerschmann and Kopinke, 2001), while the organic acid functional groups typically present in organic matter have a high affinity to attract metal cations (Zaccone *et al.*, 2009). Organic matter also plays a vital role in the reduction of metal(loid)s such as Cr^{6+}, thereby reducing their toxicity and bioavailability (Bolan *et al.*, 2003b). Another indirect effect of soil components including organic matter

is their role on limiting contaminant mass transfer. The rate of mass transfer of a contaminant from soil particles to the surrounding pore water is inversely proportional to the contaminant's soil pore water distribution coefficient (Clothier *et al.*, 2008; Menzie *et al.*, 2000). Therefore, with increasing organic matter content, retention of some metal(loid)s increases and rates of release decrease, thereby decreasing their overall bioavailability (Stokes *et al.*, 2005).

As discussed above, pH influences sorption through its effect on surface charge as quantified by cation and AECs of soils. In variable charge soils, while the AEC, a measure of available positively charged surface sites, decreases with increasing soil pH, the cation exchange capacity (CEC), a measure of negatively charged sites, increases with pH. Both AEC and CEC vary with the clay mineral content and type, organic matter, and soil pH (Bohn *et al.*, 1985). Soils with high clay content will have a high affinity to sorb cationic metal(loid) species due to high CEC, thus making contaminants less bioavailable relative to sandy soils. The AEC of most soils is small. Therefore, it is not generally considered an important parameter in assessing contaminant availability at most sites in the temperate regions. However, soils in the tropics and in volcanic and less-weathered soils such as Andepts can have a significant AEC.

In addition to soil pH, many other environmental variables influence the ion exchange characteristics of soils. These include the presence of inorganic and organic ligands that bind specifically to soil colloid surface. While the specific sorption of anions onto variable charge components has often been shown to increase the net surface charge (i.e., CEC) of soils and consequently increase the capacity of soils to bind cationic metals, sorption of cations increases the net positive charge, resulting in increased retention of anions (Bolan *et al.*, 1999). This process has been described by a number of researchers as anion-induced cation sorption (Bolan *et al.*, 1999, 1977; Wann and Uehara, 1978) and cation-induced anion retention (Bolan *et al.*, 1994; Cichota *et al.*, 2007). Metall(oid)s can also form complexes and precipitates with inorganic soil constituents, such as carbonate and phosphate minerals under certain soil conditions (Bolan *et al.*, 2003a). Carbonate- and phosphate–metal complexes have varying degrees of solubility and reactivity depending on the metal, its oxidation state, the ligand to which it is bound, and pH. Environmental managers often use changes in surface chemical properties of soils as influenced by pH and ligand ions such as P to reduce metal bioavailability in soils (Basta *et al.*, 2001; Bolan *et al.*, 2003a; Kumpiene *et al.*, 2007). Raising the soil pH using lime amendments reduces plant uptake of heavy metal such as Cd due to enhanced binding and hence reduced bioavailability of the metal (Bolan *et al.*, 2003c).

The nature of soil types varies considerably depending on the geographical location. Alfisols, Entisols, Inceptisols, Ultisols, Vertisols, and Oxisols are all commonly found in tropical and subtropical regions receiving more

than 500 mm mean annual rainfall. Landscapes throughout the tropics and subtropics are, however, dominated by Oxisols and Ultisols occupying extensive areas of potentially highly productive soils. Given the widely different surface charge and chemical properties of the soils, their ability to adsorb contaminants varies considerably. Consequently, contaminant bioavailability varies significantly with soil type due to differences in soil properties. For instance, Naidu *et al.* (2008b) examined the effect of soil types on sorption of Cd and demonstrated that soils from the temperate region consisting of 2:1 layer silicate minerals generally sorbed the highest amount of Cd while the least was recorded for an Oxisol with a pH of 5.

5.2. Plant factors

Plants are central to phytostabilization because plant characteristics regulate both the transformation of metal(loid)s and binding of soil particles. Nyer and Gatliff (1996) predict that phytoremediation will be the next hot technology for the environmental remediation field, yet they caution "... that this technology is not simply the buying of plants from the local K-mart and placing them in the soil near a contaminated site!." Subsequently, phytostabilization has been slowly adopted to remediate some contaminated sites, while the technical and commercial success of phytoextraction is conspicuously absent (Robinson *et al.*, 2009). Plants with desirable phenotypic and genotypic characteristics are selected for the sustainable management of soil remediation (Tables 5 and 6). The density, morphology, and depth to which plant roots penetrate the soil are critical to potential application of this technology. Enhancement of root biomass and morphology is therefore desirable in any phytostabilization operation. Plants with dense and deep roots that can exploit larger volumes of contaminated soils have much larger surface area, thus facilitating the stabilization of soils and enhancing the microbial volatilization of metal(loid)s in the rhizosphere. Fibrous roots offer a large surface area for contaminant absorption (facilitating phytoextraction) and plant–microbe interactions (facilitating phytovolatilization). In addition, deep-rooted plants with high transpiration rates, such as hybrid poplar, can access deeper soil depths of as much as 6 m deep (Unterbrunner *et al.*, 2007). Deep-rooted willow species have been identified to accumulate substantial amounts of Cd and Zn (Utmazian *et al.*, 2007) and hold promise for their use in phytoextraction. Granel *et al.* (2002) observed a large variation in both leaf concentration of Cd and its bioaccumulation coefficient (plant:soil concentration ratio) among 15 clones of Tangoio willow (*Salix matsudana*) which they attributed to the difference in genetically controlled, plant-mediated changes in Cd bioavailability.

Strategies to increase root biomass and to enhance root/rhizosphere associations, including mycorrhizae, have been reviewed by several authors (Cunningham *et al.*, 1997; Entry *et al.*, 1996; Morgan *et al.*, 2005; Stomp

Table 6 Some tree and shrub species used for revegetating mined land (Flege, 2000)

Latin name	Common name	Mined land
Acer pseudoplatanus	Sycamore maple	W-Europe, E-Europe
Alnus glutinosa[a,b]	European/black alder	UK, W-Europe, E-Europe, US/Canada
Alnus incana'[a,b]	White/gray alder	UK, E-Europe
Caragana arborescens[a,c]	Siberian peashrub	W-Europe, US/Canada
Eleagnus umbellata[d]	Autumn olive	W-Europe, US/Canada
Fraxinus Americana	White ash	UK, E-Europe
Fraxinus excersior	European ash	UK, W-Europe, US/Canada
Hippophae rhamnoides	Sea buckthorn	UK, W-Europe, E-Europe, Russia
Larux decudya	European larch	UK, E-Europe
Melia azedarach	Pride-of-India; mahogany tree	India, Australia
Pinus contorta	Lodgepole pine	UK, W-Europe, US/Canada
Pinus nigra	Austrian/Corsican pine	UK, US/Canada
Pinus sylvestris	Scots pine	UK, US/Canada
Populus tremiula	Aspen	UK, W-Europe, E-Europe, Russia, Ukraine, India, Australia, NZ, US/Canada
Prunus serotina	Black cherry	W-Europe, US/Canada
Quercus petraea	Durmast oak	W-Europe, E-Europe, US/Canada
Quercus robur	English/truffle/summer oak	UK, W-Europe, E-Europe
Rhus tribolata	Skunkbush sumac	W-Europe, US/Canada
Robinia pseudoacacia1	Black locust	UK, E-Europe, Ukraine, Australia, US/Canada
Rosa multiflora	Multiflora rose	W-Europe, US/Canada
Salix alba	White willow	UK, US/Canada
Sorbus aucuparia	Rowan mountain ash	UK, E-Europe

[a] Nitrogen-fixing species.
[b] Acid sensitive.
[c] Acid tolerant.
[d] Salt tolerant.

et al., 1993). Genetic engineering may provide a tool to modify root morphology and/or to identify and clone relevant enzyme-controlling genes into more deep-rooted plants. However, as demonstrated by the recent discovery of As-accumulating fern species (Francesconi *et al.*, 2002; Ma *et al.*, 2001), additional screening combined with traditional breeding also offers a promising resource for enhancing phytoextraction and associated rhizosphere capabilities (Baker and Whiting, 2002; Fitz *et al.*, 2003). However, it is unlikely that genetically modified plants that extract contaminants will find widespread use. First, the technology of phytoextraction, for which these plants would be used, is unsuitable for most contaminated sites (Robinson *et al.*, 2009), and second, environmentalists could reasonably claim that such plants represent an environmental and human health risk by facilitating the passage of toxic elements into the food chain. Modification of root morphology could change microbial associations in the rhizosphere qualitatively and quantitatively (Cunningham *et al.*, 1997). For example, a mature scotch pine has been estimated to have 50,000 m of roots with 5 million root tips. These root tips could support the growth of about 5 kg of bacteria. *Agrobacterium rhizogenes* transformation could increase the number of root tips two- to fourfold and result in enhanced microbially mediated remediation (Stomp *et al.*, 1993). This is complemented by findings that uptake of Cd from sewage sludge by *A. rhizogenes* transformed *Calystegia pepium* plants was higher than in non-transformed specimen (Tepfer *et al.*, 1989).

Among the most extreme examples of metal(loid)-tolerant plant are the so-called hyperaccumulators, which can accumulate elements such as Zn, Mn, Ni, Co, Cd, or Se at high concentrations in their above-ground biomass (Yang *et al.*, 2005). Hyperaccumulators are defined as the plant species that are capable of accumulating metal(loid)s above the threshold concentrations of 10,000 mg kg^{-1} dry weight of shoots for Zn and Mn, 1000 mg kg^{-1} for Co, Cu, Ni, As, and Se, and 100 mg kg^{-1} for Cd (Baker and Brooks, 1989; Brown *et al.*, 1994). Instead of these rather arbitrary values, the bioconcentration factor (the shoot:root ratio of metal(loid) concentration) greater than 1, which is indicating efficient root-to-shoot transportation, is now used to define hyperaccumulators (McGrath and Zhao, 2003). The major processes of metal(loid) hyperaccumulation by the plants include: (a) bioactivation of metal(loid)s in the rhizosphere through root–microbe interaction; (b) enhanced uptake by metal(loid) transporters in the plasma membranes; (c) detoxification of metal(loid)s by distributing to the apoplasts like binding to cell walls and chelation of metal(loid)s in the cytoplasm with various ligands (e.g., phytochelatins, metallothioneins, metal(loid)-binding proteins); (d) sequestration of metal(loid)s into the vacuole by tonoplast-located transporters (Yang *et al.*, 2005).

The first recognized hyperaccumulators were members of the *Brassicaceae* and *Fabaceae* families, and to date, more than 400 plant species of metal

(loid) hyperaccumulator plants have been reported in the literature (Salt *et al.*, 1998). An alternative to hyperaccumulators is the use of high biomass producing nonaccumulator plants or excluder plants, which actively restrict metal(loid) uptake into the shoots. These kinds of plants can be employed for revegetation of heavy metal(loid)-contaminated sites coupled with manipulation of soil conditions to increase the metal(loid) stabilization and improve plant growth (Pulford and Watson, 2003). Revegetation of heavy metal(loid)-contaminated sites can achieve the objectives of stabilization, pollution control, visual improvement, and removal of threats to human beings (Freitas *et al.*, 2004).

The role of hyperaccumulators in phytostabilization is unclear. Generally, hyperaccumulators have a low biomass production, are exotic to most environments, and potentially facilitate the entry of metals into the food chain. Nevertheless, the hyperaccumulator *Alyssum bertolonii* has been used successfully as a colonizing plant in mine spoil (Robinson *et al.*, 2009). Here, the desirable property of the hyperaccumulator was its ability to tolerate nutrient imbalances and high Ni concentrations in the mine spoil, while adding organic matter to the spoil, thus allowing the spontaneous colonization of other species.

The selection of plants suitable for the restoration is one of the key factors to accomplish revegetation of heavy metal(loid)-contaminated sites. Plant community tolerant to the metal(loid)s plays a major role in restoration of heavy metal(loid)-contaminated sites (Banuelos and Ajwa, 1999). Plants suitable for restoration should develop an extensive root system and a large amount of biomass while keeping the translocation of metal(loid)s from roots to shoots as low as possible in soils with high metal(loid) concentrations (Rizzi *et al.*, 2004). In addition, they must adapt to diverse site conditions, establish readily, and require little money and effort to maintain. Further, they must be able to survive and reproduce in contaminated soil (Flege, 2000).

The identification of plants which exclude heavy metal(loid)s in soils is important for phytostabilization. Metal(loid) excluders can not only survive in highly polluted soils but also take up low levels of heavy metal(loid)s even in the presence of high concentrations in soils (Baker, 1981; Wenzel *et al.*, 2003). In particular, weed species often possess stress-resistant properties compared with crops and can maintain growth under adverse water and fertilizer conditions (Wei *et al.*, 2005).

Plants possess various tolerance mechanisms to withstand metal(loid) stress. Extracellularly metal(loid) tolerance may include roles for mycorrhizae and for cell wall and extracellular exudates. Tolerance could also involve the plasma membrane, either by reducing the uptake of heavy metal(loid)s or by stimulating the efflux pumping of metal(loid)s that have entered the cytosol. A variety of potential mechanisms occur within the protoplast. The mechanisms involve the repair of stress-damaged proteins such as heat shock proteins and metallothioneins, and the chelation of metal(loid)s by organic

acids, amino acids, or peptides, or their compartmentation away from metabolic processes by transport into the vacuole (Hall, 2002).

Plant tolerance of heavy metal(loid)s may also be achieved by causing chemical changes to specific metal(loid)s, thereby decreasing their bioavailability (Chaney *et al*., 1997). Deep-rooted plants can reduce the highly toxic Cr^{6+} to Cr^{3+}, which is less soluble and therefore less bioavailable (Chaney *et al*., 1997). For example, *Eichhornia crassipes* (water hyacinth) reduced Cr^{6+} to Cr^{3+} in the fine lateral roots and transported a portion of the detoxified Cr to leaf tissues (Lytle *et al*., 1998). Similarly, Pulford *et al*. (2001) noticed that Cr was held in plant roots and poorly translocated from root to shoot whether supplied as Cr^{6+} or Cr^{3+}, which may demonstrate reduction and stabilization of Cr in the plant roots (Pulford and Watson, 2003). Lead also can be immobilized within plant roots by the formation of the lead phosphate mineral (Cotter-Howells *et al*., 1994). However, the effect of plants on the bioavailability of other metal(loid)s is uncertain (Pulford and Watson, 2003). The effect of plant roots and their interaction with rhizosphere bacteria on the chemistry and bioavailability of heavy metal(loid)s in contaminated soils is an area that requires much more study for successful restoration.

5.3. Contaminant factors

The reactions of contaminants affect their bioavailability and mobility, thereby influencing phytostabilization. Metal(loid)s introduced to soils undergo a number of reactions that include adsorption, complexation, precipitation, and reduction, which control their leaching and runoff losses, and bioavailability. Chemical interactions that contribute to metal(loid) retention by soil colloids include sorption and complexation with inorganic and organic ligands. Charged ions are attracted to charged soil surfaces by electrostatic and/or stronger covalent bonds (Mott, 1981), which can be specific or nonspecific in nature (Bolan *et al*., 1999). In nonspecific adsorption, the ion charge balances on the soil surface by electrostatic attraction, while in specific adsorption, chemical bonds form between the ions and the soil surface (Spark, 1986; Sposito, 1984).

Most metal(loid) cations are strongly retained as inner sphere complexes with variable charged surfaces by the formation of covalent bonds. Metal(loid)s can react with soil organic matter by ion exchange, complexation, and precipitation. Metal(loid)s are known to form organic complexes which affect their sorption onto soil particles (Adriano, 2001). For example, Bolan *et al*. (2003d) demonstrated that the addition of organic manures increased the complexation of Cu in soils. Additionally, they observed that while Cu^{2+} adsorption measured as the change in the total Cu in soil solution was not affected by biosolids addition, Cu complexation measured as the change in free Cu^{2+} concentration increased with increasing level of biosolids. The extent of metal

(loid)s–organic complex formation, however, varies with a number of factors including temperature, steric factors, and concentration. All these interactions are controlled by solution pH and ionic strength, the nature of the metal(loid)s species, dominant cation, and inorganic and organic ligands present in the soil solution.

At high soil pH and in the presence of SO_4^{2-}, CO_3^{2-}, OH^-, and HPO_4^{2-}, precipitation appears to be the predominant process when metal(loid) cation concentrations are high (Naidu *et al.*, 1996). This occurs when the ionic product in the solution exceeds the solubility product of that phase. In normal soils, precipitation is relatively unimportant, but in heavy metal-contaminated soils, precipitation process can play a major role in remediation, especially under alkaline conditions. Increasingly, addition of phosphate is being used to precipitate excessive levels of metals such as Zn (He *et al.*, 2005) and Pb (Park *et al.*, 2011b), although phosphate may mobilize arsenic if this is present as a co-contaminant.

Both chemical and biological redox reactions affect the bioavailability of metal(loid)s such as As, Hg, and Se. Because of the great heterogeneity in the pore space of most soils, zones of reducing and oxidizing conditions are often in close proximity to one another allowing roots to access the available forms at different points in the soil. Volatilization occurs through microbial conversion of metal(loid)s to their respective metallic, hydride, or methylated forms. These forms have low boiling points and/or high vapor pressure and are therefore susceptible for volatilization. Methylation is considered to be the major process of volatilization of As, Hg, and Se in soils and sediments, resulting in the release of poisonous methyl gas (Adriano *et al.*, 2004). Although methylation of metal(loid)s occurs through both chemical (abiotic) and biological processes, biological methylation (biomethylation) is considered to be the dominant process in soils and aquatic environments. Microorganisms in soils and sediments act as biologically active methylators. Organic matter provides the source of methyl donor for both biomethylation and abiotic methylation in soils and sediments. Selenium biomethylation is of interest because it represents a potential mechanism for the removal of Se from contaminated environments, and it is believed that methylated compounds, such as dimethyl selenide, are less toxic than dissolved Se oxyanions (Meyer *et al.*, 2007).

Contaminants affect phytostabilization by changing plant growth and associated microbial communities. Phytostabilization of mine tailings is sometimes impractical, as tailings are characterized by elevated concentrations of metals such as As, Cd, Co, Mn, Pb, and Zn, and microbial community is extremely low (Mendez and Maier, 2008). In such cases, the establishment of vegetation requires soil amendments to reduce the bioavailability of phytotoxic metal(loid)s using soil amendments. For example, Ko *et al* (2008) noted that germination of Indian mustard seeds (*Brassica juncea)* was inhibited in the presence of high levels of As^{5+} in mine tailings

and application of lime and iron oxide decreased bioavailable As concentration, thereby increasing germination.

Mine spoils are the most common environments where high metal(loid) concentrations limit plant establishment. An example is the 1.5 ha Tui Mines, Te Aroha, which has had the worst environmental effects of any New Zealand mine (Morrell *et al.*, 1996). The tailings contain 0.5% Pb and 8 mg kg^{-1} Hg. Oxidation of sulfide minerals has resulted in a pH of <3, and consequently, high concentrations of the aforementioned metals are leaching into nearby waterways (Sabti *et al.*, 2000). Vegetation has failed to establish on the tailings and there is considerable wind and water erosion, which spreads contaminated materials onto surrounding areas. Robinson and Anderson (2007) report the results of a phytostabilization field trial on these tailings. The trial involved raising the pH of the tailings with repeated lime applications, the incorporation of organic matter (mushroom compost) into the top 15 cm of the tailings, and indigenous metal-tolerant species planted. Vegetation was successfully established on the 10×10 m plot (Plate 1). This has persisted and prevented further oxidation of the sulfides beneath the plot. The roles of the plants in this phytostabilization operation are to eliminate erosion and reduce the water flux through the site and hence reduce Pb and Hg leaching.

5.4. Environmental factors

Rainfall and temperature affect phytostabilization through their effects on plant growth, contaminant reactions, and soil erosion. As most contaminated sites may not have ready access to regular water supply for irrigation, rainfall plays a vital role in the establishment of vegetation. Rainfall also controls the leaching of contaminants and erosion of soil and sediments. Temperature affects both the plant growth and soil surface characteristics such as cracking and crust formation. While cracking increases the leaching of contaminants, loose, dry, and bare soil is susceptible to wind erosion by dispersion.

Phytostabilization requires that the plants tolerate trace elements in the substrate. The species or varieties should also tolerate any nutrient imbalances in the substrate. Use of exotic species in this role is fraught, as they may establish themselves as weeds. However, exotic species are less likely to suffer from native herbivores, thus increasing growth and reducing the amount of contaminant that enters into the food chain. Competition from weeds is often more problematic than soil contaminants in phytostabilization (Dickinson *et al.*, 2009).

Each contaminated site has a unique environment. Therefore, choosing the most suitable species requires a short planting trial that tests several varieties on a small area of the site, particularly for nonsoil media such as mine spoil or biosolids.

6. Advantages and Disadvantages of Phytostabilization

Phytostabilization is considerably less expensive than other remediation technologies such as capping and soil removal (Miller and Miller, 2007). Nevertheless, phytostabilization has significant setup and ongoing costs. Phytostabilization requires that the site be assessed and the most suitable soil amendments and plant species are chosen. Thus, science costs are part of phytostabilization. Whole system models, such as the Phyto-DSS (Robinson *et al.*, 2003), can be used to calculate the impact of vegetation on the site and thus determine whether phytostabilization will meet environmental regulations. There are usually ongoing monitoring costs for phytostabilization. Phytostabilization will only be used if it satisfies environmental regulations, costs less than competing technologies, and costs less than inaction (Robinson *et al.*, 2009).

There is potential to generate income from the vegetation used in phytostabilization. Phytostabilized sites can be managed so that they produce valuable products from the biomass of the vegetation. These may be nonedible products such as timber, bioenergy, biochar, or the production of essential oils or phytochemicals. Revenue may also be obtained from carbon fixation schemes because the plants, left on the site in perpetuity, represent a small carbon sink.

Phytostabilization can be used to create an ecosystem of indigenous flora and fauna, thus adding to the ecological value of the site (Plate 3). In cases such



Plate 3 Phytostabilization of Bunker Hill, Idaho, Superfund site (courtesy Dr. Sally Brown).

as the Guadiamar river phytomanagement scheme, the vegetation used to phytostabilize the site provides a "green corridor" for migrating animals between two national parks (Dominguez *et al.*, 2010). As the site is necessarily left vegetated, it is thus more esthetically appealing than sites capped with concrete, or pits resulting from soil removal. Establishing vegetation with more than 250,000 trees, shrubs, and saltbush around a lead smelter site in Port Pirie, South Australia has been crucial in reducing Pb dust movement. Red gum trees have been planted on site and *Arundo donax* formed thick stable clumps which have ability to act as a windbreak (http://www.tenby10.com/Index).

One of the major issues with phytostabilization technology is a successful operation that entails the contaminants remain on site. Therefore, site will always be contaminated and unsuitable for other land uses. The land is no longer able to be used for food production. In contrast, some engineering technologies, such as soil replacement, can return the site to its former land use. Phytostabilization suffers from a risk of future adverse advents and thus requires ongoing monitoring. Some soil processes, such as the oxidation of carbonates, can result in a rapid drop in pH and remobilization of metal (loid)s. Extreme weather events, such as high rainfall and flooding, can result in mass migration of contaminants.

The vegetation may provide an exposure pathway for contaminants to enter food chains. Dominguez *et al.* (2010) showed that the use of *Populus alba* in the Guadiamar phytostabilization program exposes herbivores to high Cd concentrations through accumulation into the leaves.

7. Enhancement of Phytostabilization

Phytostabilization can be enhanced by increasing plant growth and altering bioavailability of metal(loid)s using both organic and inorganic amendments. Although fertilizer application increases plant growth thereby enhancing phytostabilization, this approach can lead to environmental degradation resulting from the loss of nutrients through leaching and gaseous emission. Therefore, organic amendments such as biosolids and manures and biological inoculants such as plant growth-promoting bacteria (PGPB) are used to enhance plant growth. Similarly, a number of organic and inorganic amendments are used to alter the bioavailability of metal(loid)s. This section examines the values of some of these amendments in enhancing phytostabilization technology.

7.1. Plant growth-promoting bacteria

Bacteria associated with plants may have profound effects on the plant growth and nutrition through a number of mechanisms such as increasing nutrient availability and altering root morphology and surface area.

Improvement of the interactions between plants and beneficial rhizosphere microorganisms can enhance biomass production and tolerance of the plants to heavy metal(loid)s, thereby leading to successful phytostablization (Belimov *et al.*, 2005). Although these strains are helpful and persistent in pot trial for the phytostabilization (de-Bashan *et al.*, 2010), microorganisms under field conditions might face competition problems with existing microbial communities (Sessitsch and Puschenreiter, 2008).

7.1.1. Increase in nutrients availability

Nitrogen availability is the main yield-limiting factor in plant growth, especially in contaminated sites (Mantelin and Touraine, 2004). Many of the PGPB can provide nitrogen fixed to the host plant (Mantelin and Touraine, 2004). Nitrogen deficiencies can be corrected initially by applying fertilizer, but their effects are not permanent. However, PGPB can support long-term nitrogen cycling by providing a continuous supply of nitrogen (Flege, 2000).

Sajjad *et al.* (2004) have demonstrated that nitrogen fixing and phytohormone producing bacteria *Enterobacter* sp. isolated from sugarcane have beneficial effects on the growth of micropropagated sugarcane plantlets. By using ^{15}N isotope dilution technique, maximum nitrogen fixation contribution (28% of total plant nitrogen) was detected in plantlets inoculated with bacteria (Sajjad *et al.*, 2004). Similarly Bashan *et al.* (1998) showed that diazotrophic filamentous cyanobacterium *Microcoleus chthonoplastes* inoculated onto young mangrove seedlings significantly increased the levels of total N and ^{15}N isotope in the inoculated leaves over the noninoculated plants. *Azospirillium brasilense* has been shown to stimulate N accumulation by the roots and N concentration in the tissues, thereby increasing plant growth (María *et al.*, 2002).

Application of phosphorus solubilizing bacteria, *Bacillus megatherium* var. *Phosphaticum* to soil planted with sugarcane has been shown to increase the plant available P status in the soil, thereby increasing cane yield (Sundara *et al.*, 2002). Similarly, Harris *et al.* (2006) noticed an increase in the solubilization of dicalcium phosphate with phosphate-solubilizing bacteria, which resulted in an increase in wheat grain yield. Villegas and Fortin (2002) reported that the interactions between arbuscular mycorrhizal fungi with phosphate-solubilizing bacteria such as *Pseudomonas aeruginosa* and *Pseudomonas putida* significantly increased the levels of soluble P in soil.

In addition to N and P, other micro- and macronutrients uptake can be stimulated by bacteria. Inoculation with associative rhizobacteria slightly stimulated root length and biomass of hydroponically grown Cd-treated barley seedlings. The bacteria significantly increased the total amount of nutrients such as P, Mg, Ca, Fe, Mn, and Na in roots and shoots of the Cd-treated plants. The results showed that associative bacteria were capable

of decreasing partially the toxicity of Cd for the barley plants through the improvement in uptake of nutrient elements (Belimov and Dietz, 2000).

Siderophores are low-molecular-weight Fe^{3+} coordination compounds that bacteria excrete under Fe-deficient conditions (Gadd, 1992). The elevated level of heavy metal(loid)s in soil interfere with uptake of nutrients such as Fe and P, but siderophores producing bacteria can promote plant growth by increasing nutrient uptake (Zayed and Terry, 2003). Siderophore-producing and phosphate-solubilizing isolates, *Pseudomonas* sp. and *Bacillus* sp., protected the plants against the inhibitory effects of Cr and these effects might be the results of enhanced uptake of soil minerals such as Fe and P by the plants (Rajkumar *et al*., 2006). Sharma and Johri (2003) used *Pseudomonas fluorescens* sp., which produced siderophores for maize growth promotion experiments. Inoculation of seeds with the bacteria showed significant increase in germination percentage and plant growth. Maximum shoot and root length and dry weight were observed with 10 μM Fe^{3+} along with bacterial inoculants suggesting the value of siderophores producing PGPB in enhancing crop productivity in calcareous soil system which is deficient in Fe (Sharma and Johri, 2003).

Burd *et al*. (2000) inoculated *Kluyvera ascorbata* and a siderophore overproducing mutant of this bacterium into tomato, canola, and Indian mustard seeds in Ni, Zn, and Pb-contaminated soils. In most cases, the siderophore overproducing mutant *K. ascorbata* exerted a more pronounced effect on plant growth than the wild-type bacterium. The data indicate that the ability of these bacteria to protect plants against the inhibitory effects of high concentrations of Ni, Pb, and Zn is related to the bacteria providing the plants with sufficient Fe by siderophore production (Burd *et al*., 2000).

Similar to other PGPB, siderophore-producing PGPB also can protect host plants from phytopathogenic diseases. PGPB control the damage to plants from phytopathogens by secretion of siderophores to prevent pathogens in the immediate vicinity from proliferating (Glick and Bashan, 1997). *Serratia plymuthica* isolated from soil around melon roots produced the antibiotic pyrrolnitrin, siderophores, and Indole-3-acetic acid (IAA), thereby suppressing a wide range of phytopathogenic fungi *in vitro*. Foliar application of the bacteria protected cucumber against *Botrytis cinerea* gray mold and *Sclerotinia sclerotiorum* white mold diseases of leaves under greenhouse conditions (Kamensky *et al*., 2003).

7.1.2. Alteration of root morphology

An increase in the root surface area and the volume of soil explored by the root, which leads to increased nutrient uptake, is the most commonly proposed explanation for the beneficial effects of PGPB on plant growth. The improvement in mineral nutrition promotes shoot growth and this rationale is consistent with the observation that plants inoculated with *Azopsirillum* take up N, P, K, and microelements more efficiently from

the soil (Okon and Vanderleyden, 1997). In the nutrient deficient conditions, PGPB increase the elongation rate of lateral roots resulting in a more branched root system and an increase in root surface area. This results in increased mineral uptake which, in turn, enhances shoot biomass accumulation (Lifshitz *et al.*, 1987; Mantelin and Touraine, 2004).

Soil physical parameters are critical for plant growth. Many metal(loid)-contaminated mine sites have poor soil structure, resulting in poor water infiltration or retention. Alami *et al.* (2000) demonstrated that *Rhizobium* sp. isolated from the rhizosphere of sunflower caused a significant increase in root-adhering soil per root dry mass and in soil macropore volume even in dry conditions. Further, inoculated sunflower increased nitrogen uptake, thereby promoting plant growth. Isolated strain was also able to relieve the effect of water stress on sunflower growth (Alami *et al.*, 2000).

Plants produce ethylene in response to stress (Deikman, 1997). However, high levels of ethylene lead to the inhibition of root elongation. PGPRs contain an enzyme, 1-aminocyclopropane-1-carboxylate (ACC) deaminase, that catalyzes the cleavage of ACC, which is the precursor of ethylene, and as a result, the endogenous ethylene concentration in plants is reduced (Glick *et al.*, 1998). These processes can promote plant growth by decreasing plant's ethylene level. When canola seeds were imbibed in several ACC deaminase containing strains of bacteria, the ACC levels in these roots were lowered and the growth of canola seedling roots was increased (Penrose *et al.*, 2001). Hall *et al.* (1996) demonstrated that PGPB promote root elongation in a variety of plants. Seeds of canola, lettuce, tomato, and wheat when inoculated with PGPB (*P. putida*) increased the root lengths. These observations are consistent with a model in which promotion of root growth by *P. putida* is a consequence of inhibition of ethylene production within the developing seedling (Hall *et al.*, 1996).

ACC deaminase activity can not only improve root growth but also protect plant from pathogenic disease. Transformed *Pseudomonas fluorescens* strains with ACC deaminase activity improved its ability to protect cucumber against Pythium damping-off, and potato tubers against Erwinia soft rot in small completely sealed containers (Wang *et al.*, 2000).

Production of the phytohormone IAA is widespread among bacteria that inhabit the rhizosphere of plants (Patten and Glick, 1996). An Ni tolerant *Bacillus subtilis* produced substantial amount of IAA during stationary phase of growth in the medium and showed time-dependent increase in IAA production. Enhanced production of IAA (55 $\mu g\ mL^{-1}$) was noticed in the presence of tryptophan (500 $\mu g\ mL^{-1}$). The phytohormone IAA production offers great promise for sustaining the increased crop productivity (Zaidi *et al.*, 2006). In addition, Cd-tolerant bacterial strains, *Variovorax paradoxus* and *Rhodococcus* sp., isolated from the rhizosphere of Indian mustard seedlings grown in highly Cd-contaminated sites produced IAA. The bacteria also showed increased tolerance to other metal(loid)s including

Zn, Cu, Ni, and Co. These strains were capable of stimulating root elongation of *B. juncea* seedlings either in the presence or absence of toxic Cd concentrations (Belimov *et al.*, 2005), and *Pseudomonas* sp. and *Bacillus* sp. facilitated rape growth (Sheng and Xia, 2006).

The primary roots of canola seedlings from seeds treated with wild-type *P. putida* were on average 35–50% longer than the roots from seeds treated with the IAA-deficient mutant and the roots from uninoculated seeds, and these results suggest that bacterial IAA plays a major role in the development of the host plant root system (Patten and Glick, 2002). Rajkumar *et al.* (2006) isolate Cr^{6+} resistant PGPB, *Pseudomonas* sp. from heavy metal(loid) contaminated soils. They noticed that the inoculation of bacteria protected the plants against the inhibitory effects of Cr and promoted the growth of Indian mustard and this effect was higher in IAA producing bacteria than IAA nonproducing bacteria.

Gibberellins are phytohormones that control a number of developmental and physiological processes in plants (Crozier *et al.*, 2000) and affect root elongation (Tanimoto, 1987), promotion of root growth, and root hair abundance (Bottini *et al.*, 2004). Bacteria and fungi also produce Gibberellins. *Bacillus pumilus* and *Bacillus licheniformis,* isolated from the rhizosphere of alder, had a strong growth-promoting activity. Gibberellins (GA_1, GA_3, GA_4, and GA_{20}) in extracts of bacterial media were detected by full-scan gas chromatography–mass spectrometry analyses.

7.2. Inorganic amendments

A number of inorganic amendments such as liming materials, phosphate compounds, and clay materials are used for immobilizing heavy metal(loid)s and improving soil conditions to facilitate revegetation of contaminated soils (Kumpiene *et al.*, 2007). For example, the addition of liming materials is a common practice to overcome plant growth constrains relating to soil acidification. Normally, as the pH decreases, the mobility of some metal(loid)s is elevated. The solubility of Zn and Ni in dredged sediment increased when the pH was less than 6, pH 4 for Cd, pH 6 for Co, and pH 2 for Cu and Pb (Tack *et al.*, 1996). The addition of lime as ground limestone not only raises pH but also renders metal(loid)s insoluble, thus reducing their bioavailability to plants (Down, 1975).

Lime is effective in reducing the phytoavailability of Cd and Cr^{3+} (Bolan and Duraisamy, 2003). Sugar beet lime, a residual material from the sugar manufacturing process with 70–80% (dry basis) of $CaCO_3$ and biosolids compost, reduced $CaCl_2$-extractable Cd, Cu, and Zn concentrations. This behavior seems to be related to the pH increase as it is well known that increasing the pH of the soil leads to a decrease in metal(loid) mobility. Soluble Cd, Cu, and Zn concentrations in soils are often found to be negatively correlated with pH values (Burgos *et al.*, 2006).

Gray *et al.* (2006) evaluated the effectiveness of lime to reduce Pb availability, and the treatment reduced Pb concentration of pore water and NH_4NO_3-extractable Pb concentration of the amended soil. Three soil amendments (red mud, beringite, and lime) were applied to metal(loid)-contaminated soil. Treatment of lime and red mud reduced Pb concentrations in plants. Treatment applications shifted the distribution of Pb from the exchangeable fraction to the carbonate and oxide fraction and decreased acid extractability of Pb. Lead solubility is generally very low in nonacidic soils, and the amendments used can only slightly reduce its mobility (McGrath *et al.*, 2002).

Inorganic amendments such as quarry waste, pulverized refuse, and pulverized fuel ash have also been used to improve substrate characteristics (Wong, 2003). For instance, expanded clay and N and P fertilizer increased the plant biomass of *Andropogon gerardii* in mine tailings (Hetrick *et al.*, 1994). Lead immobilization efficiency in artificially polluted soil with modified clay was 93% for Mn-montmorillonite, 86% for Mn-diatomite, 81% for Fe-montmorillonite, and 80% for Fe-diatomite. The results of sequential extraction of Pb from soil after immobilization with modified clays indicated that mobile fraction (i.e., exchangeable and carbonate fraction) decreased as contact time increased, while less mobile (i.e., reducible) fraction increased from 27% to 60% of the total amount extracted (Park and Shin, 2006). Bolan and Duraisamy (2003) demonstrated that P compounds immobilized Cd through phosphate-induced metal(loid) adsorption and the formation of cadmium–phosphate complex. Similarly, Park *et al.* (2011b) have demonstrated the potential value of both soluble and insoluble P compounds in the immobilization of Pb, thereby reducing its bioavailability and toxicity.

Some minerals are known to have a metal(loid) immobilizing capacity. The application of synthetic zeolite pellets to Cd-contaminated soils has been shown to significantly reduce the concentrations of Cd in the roots and shoots of a range of crop plants (Gworek, 1992). The addition of beringite, a modified aluminosilicate, resulted in a complete disappearance of visual and metabolic symptoms of metal(loid) phytotoxicity by metal(loid) immobilization. The high metal(loid) immobilizing capacity of beringite is based on chemical precipitation, ion exchange, and crystal growth (Vangronsveld *et al.*, 1995b).

When combined with compost, inorganic metal(loid) immobilizing amendments resulted in better plant responses when compared to the addition of inorganic amendments alone. Compost, beringite, and steel shots treatment in metal(loid)-contaminated sandy soil reduced phytotoxicity and metal(loid) accumulation in grasses. This may be attributed to an increased efficiency of metal(loid) binding on Fe or Mn oxides due to the high pH and precipitation of Fe oxides on clay particles induced by the beringite (Ruttens *et al.*, 2006). Hydrous manganese oxides reduced Cd or

Pb transfer from soil to soil solution and their entry into the food chain via plant uptake. This material would be promising for restoration of Cd and Pb-contaminated soils (Mench *et al.*, 1994).

Castaldi *et al.* (2005) amended Pb-contaminated soils with zeolite, compost, and $Ca(OH)_2$. The amendments increased the residual fraction of heavy metal(loid)s in the soils and decreased the Pb uptake by white lupin (*Lupinus albus* L., cv. Multitalia). The concentration of Pb in the aerial part of plants grown in compost soil was 87% lower than in the control sample. All treatments with amendments had higher plant yield than control, especially, compost and $Ca(OH)_2$. Similarly, Ciccu *et al.* (2003) used red mud, bauxite ore processing waste, and/or fly ash produced by coal-fired power stations to immobilize the heavy metal(loid)s in severely contaminated soils. Eluted Pb concentration from red mud and fly ash amended soil was reduced by 59–97% compared to the control.

7.3. Organic amendments

Organic materials such as sewage sludge, domestic refuse, peat, and topsoil improve the physical nature of soils by increasing water holding capacity and also provide plant nutrients in a slow-release form (Park *et al.*, 2011b; Tordoff *et al.*, 2000; Wong, 2003). In particular, organic amendments have a high CEC and can form stable organic–heavy metal(loid) complexes, thereby lowering metal(loid) availability in contaminated soil (Hetrick *et al.*, 1994). Cerezo *et al.* (1999) have shown that the treatment of a clay quarry with sewage sludge increased the pH and organic matter content and decreased the available heavy metal(loid)s over time due to complexation and immobilization processes.

Rizzi *et al.* (2004) noticed that compost treatment in soils from an Italian mining area improved soil physical characteristics such as particle size distribution, cracking pattern, and porosity. The development of better soil structural characteristics may prevent the dispersion of metal(loid)-contaminated particles by formation of water-stable aggregates. Compost addition improved the growth of *Lolium italicum* and *Festuca arundinacea* and decreased Zn and Pb content in stems and leaves.

The addition of manure byproducts increases the complexation of metal(loid)s in soils, the extent of which is related to the amount of dissolved organic carbon (DOC; Hesterberg *et al.*, 1993). The mobility of metal(loid)s may be facilitated greatly in soils receiving DOC because of the increased concentration of soluble metal(loid)–organic complex in solution and decrease in metal(loid) sorption (Bolan *et al.*, 2011). Accordingly, in soils containing large amounts of organic matter, such as pasture soils, muck, peaty soils, and organic manure-amended soils, only a small proportion of soil solution metal(loid) remains as free metal(loid) ion and a large portion is complexed with DOC. For example, using cation-exchange column

experiments as well as anodic stripping voltametry measurements, del Castilho *et al.* (1993) observed that 30–70% of the dissolved Cu and all Cd in soils treated with cattle manure slurry was bound in relatively fast dissociating organic–metal(loid) complexes.

Although a wide variety of organic compounds in DOC are involved in the formation of soluble complexes with metal(loid)s (Daum and Newland, 1982), Zhou, and Wong (2001) and del Castilho *et al.* (1993) observed that the low-molecular-weight fractions, such as hydrophilic bases in biosolids and manures, have strong affinity for forming soluble complexes with Cd, Cu, and Zn. Thus, the formation of soluble aqueous metal(loid)–organic and, to a lesser extent, metal(loid)–inorganic complexes is expected to dominate the solution chemistry of metal(loid)s in manure-amended soils (Hesterberg *et al.*, 1993).

A number of studies have shown that addition of organic matter-rich soil amendments enhances the reduction or transformation of certain metal(loid)s, such as Cr and Se (Alexander, 1999; Frankenberger and Losi, 1995). For example, Ajwa *et al.* (1998) noticed enhanced loss of Se in the presence of organic amendments such as manure, which they attributed to manure-facilitated volatilization due to the reduction of Se. Similarly, Losi *et al.* (1994) and Higgins *et al.* (1998) have noticed that the addition of cattle manure resulted in the reduction of Cr^{6+} to less-toxic and less-mobile Cr^{3+} (Fig. 5). Various reasons could be attributed to the enhanced reduction (i.e., lowering in valency) of Cr^{6+} in the presence of the organic manure

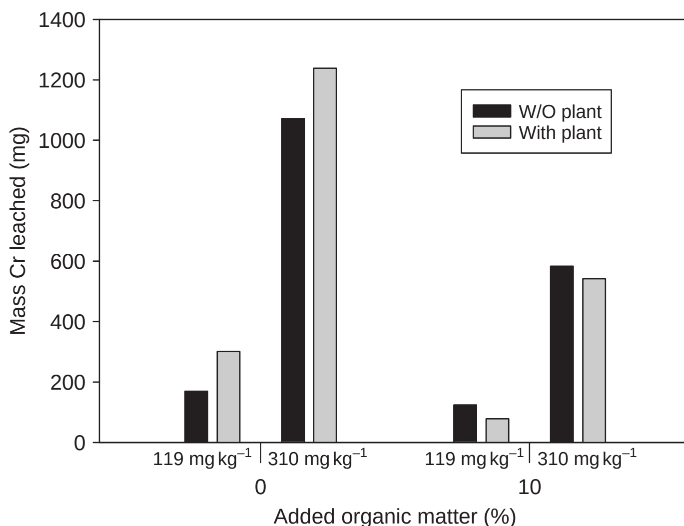


Figure 5 Effect of organic matter and plants on Cr leaching with low (119 mg kg^{-1}) Cr addition and high (310 mg kg^{-1}) Cr addition (Banks *et al.*, 2006).

compost, including the supply of carbon and protons and the stimulation of microorganisms that mediate and facilitate the reduction of Cr^{6+} to Cr^{3+} (Losi *et al.*, 1994).

At the same level of total organic carbon addition, Bolan *et al.* (2003b) observed significant difference in the extent of Cr^{6+} reduction between various organic manure composts. The extent of Cr^{6+} reduction increased with increasing level of DOC added through manure addition, which has been identified to facilitate the reduction of Cr^{6+} to Cr^{3+} in soils (Jardine *et al.*, 1999). For example, the hydroquinone groups in organic matter have been identified as the major source of electron donor for the reduction of Cr^{6+} to Cr^{3+} in soils (Elovitz and Fish, 1995).

The increase in Cr^{6+} reduction in the presence of organic manure addition may also result from enhanced microbial activity. Although Cr^{6+} reduction can occur through both chemical and biological processes, the biological reduction is considered to be the dominant process in most arable soils which are low in Fe^{2+} ion. It has been shown that the addition of manure compost caused a larger increase in the biological reduction than chemical reduction of Cr^{6+}, indicating that the supply of microorganisms is more important than the supply of organic carbon in enhancing the reduction of Cr^{6+} when compost is added (Banks *et al.*, 2006; Chiu *et al.*, 2009; Losi *et al.*, 1994). Addition of manure compost has often been shown to increase the microbial activity of soil, as measured by increased respiration and enzymatic activities (Chang *et al.*, 2008; Kanazawa *et al.*, 1988; Saha *et al.*, 2008; Tejada, 2009). This arises from both increased supply of carbon and nutrients, such as nitrogen, phosphorus, and sulfur (Tejada *et al.*, 2006; Wardle, 1992).

7.4. Geotextile capping

Geosynthetics are thin polymeric materials that are widely used in geotechnical, environmental, and hydraulic applications (Bouazza *et al.*, 2006). A geotextile is a geosynthetic fabricated to be permeable and can be classified by the way they are manufactured as either woven or nonwoven (Koerner and Koerner, 2006). Nonwoven geotextiles are felt-like materials which are formed by a random placement of threads and do not have any visible thread pattern (Koerner and Koerner, 2006). They can also be used in canals and channels that are downstream from dredging operations, such as for the dewatering of sediments in geotubes (Moo-Young and Tucker, 2002) and other geotextile containers in one- (Kutay and Aydilek, 2004) and two-layer systems (Kutay and Aydilek, 2005). Geotextiles have been used along shorelines and landfill sites to reduce the introduction of suspended material through erosion (e.g., Bouazza and Vangpaisal, 2007; Brachman and Gudina, 2008).

Various reactive materials (e.g., activated carbon, apatite, organoclay, zeolite, zero-valent iron) used for the immobilization of contaminants may be applicable to *in situ* capping using geotextile mat. For example, geosynthetic clay liners (GCLs) consisting of a thin layer of bentonite supported by one or two layers of geosynthetics are now well recognized as an alternative to traditional compacted clay liners. A number of studies have established the use of clays for attenuating metallic contaminants. A reactive material mat will have several advantages over loose placement of reactive materials, including (Olsta *et al.*, 2006): (1) uniform and verifiable mass per area placement of reactive or adsorptive material; (2) ability to mix reactive or adsorptive materials in defined proportions; (3) easy separation of the reactive material from the contaminated sediment and cover material; (4) providing barrier to biointrusion, resistance to uplift and differential settlement, and stability on sloped areas. Geotextiles also help to separate micropollutants such as Cd, Zn, and Cu from the underlying soil in landfill sites, therefore preventing groundwater from becoming contaminated and are also effective in attenuating metals from mining leachates (Lange *et al.*, 2007).

8. Conclusions and Future Research Needs

Phytostabilization is primarily aimed at containing the mobility of contaminants through their immobilization within the root zone of plants and "holding" soil and sediments, thereby preventing off-site contamination through their migration via wind and water erosion and leaching, and soil dispersion. Phytostabilization also results in the removal of contaminants through plant uptake and volatilization and this technology can be enhanced by using soil amendments that are effective in the immobilization of metal(loid)s. This technique is readily suited to monitor natural attenuation of contaminated sites which is employed within the context of a carefully controlled site-specific cleanup strategy. For example, this technology (i.e., phytocapping) has been found to be very effective in mitigating leachate and greenhouse gas generation in the management of landfill sites. The main advantage of this technology is that it reduces the mobility, and therefore, the risk of contaminants without necessarily removing them from their source location. Further, this technology does not generate contaminated secondary waste that needs treatment and also provides ecosystem development to achieve biodiversity corridors. However, since the contaminants are left in place, the site requires regular monitoring in order to maintain the stabilizing conditions. If soil amendments are used to enhance immobilization, they may need to be periodically reapplied to maintain the effectiveness of the phytoimmobilization.

Given the current knowledge of phytostabilization technology, the following research areas could be pursued:

- Impact of plant roots and associated microorganisms on the nature and extent of immobilization, volatilization, and methylation of metal(loid)s (Hg, Pb, As, and Se).
- Effect of various carbon fractions (e.g., DOM) on sorption/desorption of metal(loid)s and their transport to soil strata, streams, and lakes.
- Impact of harvesting and natural death of plants on the solubility, mobility, and dispersion of contaminants.
- Nature and extent of soil mineral-OM-microbe interactions as influenced by environmental factors such as land use and acid rain, and edaphic factors such as soil type and clay mineralogy.
- Nature of microbial communities as affected by OM dynamics and their role on the degradation of OM.
- Effect of heterogeneity on the performance of the system. Both contaminants and plant nutrients are distributed heterogeneously in soil. Avoidance/foraging of hotspots may have a large effect on plant uptake and leaching.
- Modeling phytostabilization systems. Since plants on each contaminated site comprise a unique ecosystem, experiments are required to determine both the feasibility and costs of phytostabilization. Full-system models could reduce these costs.

ACKNOWLEDGMENTS

We would like to thank CRC CARE for providing funding (No 2-3-09-07/08) and Gyeongnam National University of Science and Technology to undertake research on landfill site remediation; part of the chapter was derived from these projects.

REFERENCES

Adriano, D. C. (2001). Trace Elements in Terrestrial Environments; Biogeochemistry, Bioavailability and Risks of Metals. 2nd edn., Springer, New York, NY.

Adriano, D. C., Wenzel, W. W., Vangronsveld, J., and Bolan, N. S. (2004). Role of assisted natural remediation in environmental cleanup. *Geoderma* **122,** 121–142.

Aira, M., Gómez-Brandón, M., Lazcano, C., and Domínguez, J. (2010). Plant genotype strongly modifies the structure and growth of maize rhizosphere microbial communities. *Soil Biol. Biochem.* **42,** 2276–2281.

Ajwa, H. A., Banuelos, G. S., and Mayland, H. F. (1998). Selenium uptake by plants from soils amended with inorganic and organic materials. *J. Environ. Qual.* **27,** 1218–1227.

Alami, Y., Achouak, W., Marol, C., and Heulin, T. (2000). Rhizosphere soil aggregation and plant growth promotion of sunflowers by an exopolysaccharide-producing *Rhizobium* sp. strain isolated from sunflower roots. *Appl. Environ. Microbiol.* **66,** 3393–3398.

Alexander, M. (1999). Biodegradation and Bioremediation. 2nd edn., CA Academic Press, San Diego.

Anderson, T. A., Guthrie, E. A., and Walton, B. T. (1993). Bioremediation in the rhizosphere. *Environ. Sci. Technol.* **27,** 2630–2636.

Ashwath, N., and Venkatraman, K. (2010). Phytocapping: An alternative technique for landfill remediation. *Int. J. Environ. Waste Manage.* **6,** 51–70.

Auxtero, E., Madeira, M., and Sousa, E. (2004). Variable charge characteristics of selected Andisols from the Azores, Portugal. *Catena* **56,** 111–125.

Awad, F., Romheld, V., and Marschner, H. (1994). Effect of root exudates on mobilization in the rhizosphere and uptake of iron by wheat plants. *Plant Soil* **165,** 213–218.

Baker, A. J. M. (1981). Accumulators and excluders—Strategies in the response of plants to heavy metals. *J. Plant Nutr.* **3,** 643–654.

Baker, A. J. M., and Brooks, R. R. (1989). Terrestrial higher plants which hyperaccumulate metallic elements—A review of their distribution, ecology and phytochemistry. *Biorecovery* **1,** 81–126.

Baker, A. J. M., and Whiting, S. N. (2002). In search of the Holy Grail—A further step in understanding metal hyperaccumulation? *Sci. Total Environ.* **155,** 1–4.

Banks, M. K., Schwab, A. P., and Henderson, C. (2006). Leaching and reduction of chromium in soil as affected by soil organic content and plants. *Chemosphere* **62,** 255–264.

Banuelos, G. S., and Ajwa, H. A. (1999). Trace elements in soils and plants: An overview. *J. Environ. Sci. Health A Tox. Hazard Subst. Environ. Eng.* **34,** 951–974.

Banuelos, G. S., and Lin, Z. Q. (2007). Acceleration of selenium volatilization in seleniferous agricultural drainage sediments amended with methionine and casein. *Envrion. Pollut.* **150,** 306–312.

Barton, C., Marx, D., Adriano, D. C., Koo, B. J., Newman, L., Czapka, S., and Blake, J. (2005). Phytostabilization of a landfill containing coal combustion waste. *Environ. Geosci.* **12,** 251–265.

Bashan, Y., Puente, M. E., Myrold, D. D., and Toledo, G. (1998). In vitro transfer of fixed nitrogen from diazotrophic filamentous cyanobacteria to black mangrove seedlings. *FEMS Microbiol. Ecol.* **26,** 165–170.

Basta, N. T., Gradwohl, R., Snethen, K. L., and Schroder, J. L. (2001). Chemical immobilisation of lead, zinc and cadmium in smelter-contaminated sols using biosolids and rock phosphate. *J. Environ. Qual.* **30,** 1222–1230.

Belimov, A. A., and Dietz, K. (2000). Effect of associative bacteria on element composition of barley seedling grown in solution culture at toxic cadmium concentrations. *Microbiol. Res.* **155,** 113–121.

Belimov, A. A., Hontzeas, N., Safronova, V. I., Demchinskaya, S. V., Piluzza, G., Bullitta, S., and Glick, B. R. (2005). Cadmium-tolerant plant growth-promoting bacteria associated with the roots of Indian mustard (*Brassica juncea* L. Czern.). *Soil Biol. Biochem.* **37,** 241–250.

Berti, W. R., and Cunningham, S. D. (2000). Phytostabilization of metals. *In* "Phytoremediation of Toxic Metals: Using Plants to Clean Up the Environment" (I. B. Raskin and D. Ensley, Eds.), pp. 71–88. Wiley, New York.

Bohn, H., McNeal, B., and O'Connor, G. (1985). *In* "Soil Chemistry", 2nd edn., Wiley, New York.

Bolan, N. S., and Duraisamy, V. P. (2003). Role of inorganic and organic soil amendments on immobilisation and phytoavailability of heavy metals: A review involving specific case studies. *Aust. J. Soil Res.* **41,** 533–555.

Bolan, N. S., and Hedley, M. J. (2003). The role of carbon, nitrogen and sulphur in soil acidification. *In* "Hand Book of Soil Acidification" (Z. Rengel, Ed.), pp. 29–56. Marcel and Dekker Inc., New York.

Bolan, N. S., Naidu, R., Mahimairaja, S., and Baskaran, S. (1994). Influence of low molecular weight organic acid on the solubilization of phosphorus in soils. *Biol. Fertil. Soils* **18,** 311–319.
Bolan, N. S., Elliott, J., Gregg, P. E. H., and Weil, S. (1996). Rhizosphere induced dissolution of phosphate rocks in soils. *Biol. Fertil. Soils* **24,** 169–174.
Bolan, N. S., Naidu, R., Syers, J. K., and Tillman, R. W. (1999). Surface charge and solute interactions in soils. *Adv. Agron.* **67,** 88–141.
Bolan, N. S., Adriano, D. C., and Naidu, R. (2003a). Role of phosphorus in (im)mobilization and bioavailability of heavy metals in the soil-plant system. *Rev. Environ. Contam. Toxicol.* **177,** 1–44.
Bolan, N. S., Adriano, D. C., Natesan, R., and Koo, B. J. (2003b). Effects of organic amendments on the phytoavailability of chromate in mineral soil. *J. Environ. Qual.* **32,** 120–128.
Bolan, N. S., Adriano, D. C., Mani, P., Duraisamy, A., and Arulmozhiselvan, S. (2003c). Immobilization and phytoavailability of cadmium in variable charge soils: II effect of lime addition. *Plant Soil* **250,** 187–198.
Bolan, N. S., Adriano, D. C., Mani, S., and Khan, A. R. (2003d). Adsorption, complexation and phytoavailability of copper as influenced by organic manure. *Environ. Toxicol. Chem.* **22,** 450–456.
Bolan, N. S., Adriano, D., Senesi, N., Kunhikrishnan, A., James, T., and McDowell, R. (2011). Dissolved organic carbon: Biogeochemistry, dynamics and agro-environmental significance in soils. *Adv. Agron.* **110,** 1–75.
Bolland, M. D. A., Posner, A. M., and Quirk, J. P. (1977). Zinc adsorption by goethite in the absence and presence of phosphate. *Aust. J. Soil Res.* **15,** 279–286.
Bottini, R., Cassan, F., and Piccoli, P. (2004). Gibberellin production by bacteria and its involvement in plant growth promotion and yield increase. *Appl. Microbiol. Biotechnol.* **65,** 497–503.
Bouazza, A., and Vangpaisal, T. (2007). Gas transmissivity at the interface of a geomembrane and the geotextile cover of a partially hydrated geosynthetic clay liner. *Geosynth. Int.* **14,** 316–319.
Bouazza, A., Freund, M., and Nahlawl, H. (2006). Water retention of nonwoven polyester geotextiles. *Polym. Test.* **25,** 1038–1043.
Brachman, R. W. I., and Gudina, S. (2008). Gravel contacts and geomembrane strains for a GM/CCL composite liner. *Geotext. Geomembr.* **26,** 448–459.
Bronick, C. J., and Lal, R. (2005). Soil structure and management: A review. *Geoderma* **124,** 3–22.
Brown, S. L., Chaney, R. L., Angle, J. S., and Baker, A. J. M. (1994). Phytoremediation potential of *Thlaspi caerulescens* and Bladder Campion for zinc- and cadmium-contaminated soil. *J. Environ. Qual.* **23,** 1151–1157.
Burd, G. I., Dixon, D. G., and Glick, B. R. (2000). Plant growth-promoting bacteria that decrease heavy metal toxicity in plants. *Can. J. Microbiol.* **46,** 237–245.
Burgos, P., Madejon, E., Perez-De-Mora, A., and Cabrera, F. (2006). Spatial variability of the chemical characteristics of a trace-element-contaminated soil before and after remediation. *Geoderma* **130,** 157–175.
Cakmak, I., Gulut, K. Y., Marschner, H., and Graham, R. D. (1994). Effect of zinc and iron-deficiency on phytosiderophore release in wheat genotypes differing in zinc efficiency. *J. Plant Nutr.* **17,** 1–17.
Cakmak, I., Sari, N., Marschner, H., Ekiz, H., Kalayci, M., Yilmaz, A., and Braun, H. J. (1996). Phytosiderophore release in bread and durum wheat genotypes differing in zinc efficiency. *Plant Soil* **180,** 183–189.
Castaldi, P., Santona, L., and Melis, P. (2005). Heavy metal immobilization by chemical amendments in a polluted soil and influence on white lupin growth. *Chemosphere* **60,** 365–371.

Cerezo, L. M. L., Marcos, F. M. L., and Rodriguez, A. E. (1999). Heavy metals in mine soils amended with sewage sludge. *Land Degrad. Dev.* **10,** 555–564.

Chaney, R. L., Malik, M., Li, Y. M., Brown, S. L., Brewer, E. P., Angle, J. S., and Baker, A. J. (1997). Phytoremediation of soil metals. *Curr. Opin. Biotechnol.* **8,** 279–284.

Chang, A. C., Page, A. L., and Koo, B. J. (2002). Biogeochemistry of phosphorus, iron, and trace elements in soils as influenced by soil-plant-microbial interactions. *Dev. Soil Sci.* **28,** 43–57.

Chang, E. H., Chung, R. S., and Wang, F. N. (2008). Effect of different types of organic fertilizers on the chemical properties and enzymatic activities of an oxisol under intensive cultivation of vegetables for 4 years. *Soil Sci. Plant Nut.* **54,** 587–599.

Chen, L., Huang, Z., Gong, J., Fu, B., and Huang, Y. (2007). The effect of land cover/vegetation on soil water dynamic in the hilly area of the loess plateau, China. *Catena* **70,** 200–208.

Cheng, S. F., and Hseu, Z. Y. (2002). In-situ immobilization of cadmium and lead by different amendments in two contaminated soils. *Water Air Soil Pollut.* **140,** 73–84.

Chiou, C. T., Porter, P. E., and Shoup, T. D. (1984). Partition equilibria of nonionic organic-compounds between soil organic-matter and water. *Environ. Sci. Technol.* **18,** 295–297.

Chiu, C. C., Cheng, C. J., Lin, T. H., Juang, K. W., and Lee, D. Y. (2009). The effectiveness of four organic matter amendments for decreasing resin-extractable Cr (VI) in Cr (VI)-contaminated soils. *J. Hazard. Mater.* **161,** 1239–1244.

Ciccu, R., Ghiani, M., Serci, A., Fadda, S., Peretti, R., and Zucca, A. (2003). Heavy metal immobilization in the mining-contaminated soils using various industrial wastes. *Miner. Eng.* **16,** 187–192.

Cichota, R., Vogeler, I., Bolan, N. S., and Clothier, B. E. (2007). Simultaneous adsorption of calcium and sulfate and its effect on their movement. *Soil Sci. Soc. Am.* **71,** 703–710.

Clothier, B. E., and Green, S. R. (1997). Roots: The big movers of water and chemical in soil. *Soil Sci.* **162,** 534–543.

Clothier, B. E., Green, S. R., Robinson, B. R., Thaylakumaran, T., Scotter, D. R., Vogeler, I., Mills, T. M., Deurer, M., van der Velde, M., and Granel, Th. (2008). Contaminants in the rootzone: Bioavailability, uptake and transport, and their implications for remediation. *In* "Chemical Bioavailability in Terrestrial Environment" (R. Naidu, Ed.), pp. 633–655. Elsevier, Amsterdam.

Conesa, H. M., García, G., Faz, Á., and Arnaldos, R. (2007). Dynamics of metal tolerant plant communities' development in mine tailings from the Cartagena-La Unión Mining District (SE Spain) and their interest for further revegetation purposes. *Chemosphere* **68,** 1180–1185.

Conesa, H. M., Moradi, A. B., Robinson, B. H., Kühne, G., Lehmann, E., and Schulin, R. (2009). Response of native grasses and *Cicer arietinum* to soil polluted with mining wastes: Implications for the management of land adjacent to mine sites. *Environ. Exp. Bot.* **65,** 198–204.

Cotter-Howells, J., and Caporn, S. (1996). Remediation of contaminated land by formation of heavy metal phosphates. *Appl. Geochem.* **11,** 335–342.

Cotter-Howells, J. D., Champness, P. E., Charnock, J. M., and Pattrick, R. A. (1994). Identification of pyromorphite in mine-waste contaminated soils by ATEM and EXAFS. *Eur. J. Soil Sci.* **45,** 393–402.

Crozier, A., Kamiya, Y., Bishop, G., and Yokota, T. (2000). Biosynthesis of hormones and elicitor molecules. *In* "Biochemistry and Molecular Biology of Plants" (B. B. Buchanan, W. Gruissem, and R. L. Jones, Eds.), pp. 850–929. American Society of Plant Physiologists, Rockville.

Cunningham, S. D., Shann, J. R., Crowley, D. E., and Anderson, T. A. (1997). Phytoremediation of contaminated water and soil. *In* "Phytoremediation of Soil Water

Contaminants" (E. L. Kruger, T. A. Anderson, and J. R. Coats, Eds.), pp. 2–17. American Chemical Society, Washington, DC.

Daum, K. A., and Newland, L. W. (1982). Complexing effects on behavior of some metals. *In* "The Hand Book of Environmental Chemistry: Reactions and Processes" (O. Huntzinger, Ed.), pp. 129–140. Springer-Verlag, New York.

de Knecht, J. A., van Dillen, M., Koevoets, P. L. M., Schat, H., Verkleij, J. A. C., and Ernst, W. H. O. (1994). Phytochelatins in cadmium-sensitive and cadmium-tolerant *Silene vulgaris* (chain length distribution and sulfide incorporation). *Plant Physiol.* **104,** 255–261.

De Souza, M. P., Lytle, C. M., Mulholland, M. M., Otte, M. L., and Terry, N. (2000). Selenium assimilation and volatilization from dimethylselenoniopropionate by Indian mustard. *Plant Physiol.* **122,** 1281–1288.

De Souza, M. P., Pickering, I. J., Walla, M., and Terry, N. (2002). Selenium assimilation and volatilization from selenocyanate-treated Indian mustard and muskgrass. *Plant Physiol.* **128,** 625–633.

de-Bashan, L. E., Hernandez, J. P., Nelson, K. N., Bashan, Y., and Maier, R. M. (2010). Growth of quail bush in acidic, metalliferous desert mine tailings: Effect of *Azospirillum brasilense* Sp6 on biomass production and rhizosphere community structure. *Microb. Ecol.* **60,** 1–13.

Deikman, J. (1997). Molecular mechanisms of ethylene regulation of gene transcription. *Physiol. Plantarum.* **100,** 561–566.

del Castilho, P., Chardon, W. J., and Salomons, W. (1993). Influence of cattle-manure slurry application on the solubility of cadmium, copper, and zinc in a manure acidic, loamy-sand soil. *J. Environ. Qual.* **22,** 689–697.

Dessureault-Rompré, J., Luster, J., Schulin, R., Tercier-Waeber, M. L., and Nowack, B. (2010). Decrease of labile Zn and Cd in the rhizosphere of hyperaccumulating *Thlaspi caerulescens* with time. *Environ. Pollut.* **158,** 1955–1962.

Díaz, G., Azcón-Aguilar, C., and Hornubia, M. (1996). Influence of arbuscular mycorrhizae on heavy metal (Zn and Pb) uptake and growth of *Lygeum spartum* and *Anthyllis cystoides*. *Plant Soil* **180,** 241–249.

Dickinson, N., Baker, A., Doronila, A., Laidlaw, S., and Reeves, R. (2009). Phytoremediation of inorganics: Realism and synergies. *Int. J. Phytoremediation* **11,** 97–114.

Dominguez, M. T., Maranon, T., Murillo, J. M., Schulin, R., and Robinson, B. H. (2010). Nutritional status of Mediterranean trees growing in a contaminated and remediated area. *Water Air Soil Pollut.* **205,** 305–321.

Down, C. G. (1975). Problems in vegetating metal-toxic mine wastes. *In* "Minerals and the Environment, Proceedings of an International Symposium London" (M. J. Jones, Ed.), pp. 395–408. Institute of Mining and Metallurgy, London.

Duckart, E. C., Waldron, L. J., and Donner, H. E. (1992). Selenium uptake and volatilization from plants growing in soil. *Soil Sci.* **153,** 94–99.

Duqučne, L., Vandenhove, H., Tack, F., Meers, E., Baeten, J., and Wannijn, J. (2009). Enhanced phytoextraction of uranium and selected heavy metals by Indian mustard and ryegrass using biodegradable soil amendments. *Sci. Total Environ.* **407,** 1496–1505.

Elovitz, M. S., and Fish, W. (1995). Redox interactions of Cr(VI) and substituted phenols: Products and mechanisms. *Environ. Sci. Technol.* **29,** 1933–1943.

Entry, J. A., Vance, N. A., Hamilton, M. A., Zabowsky, D., Watrud, L. S., and Adriano, D. C. (1996). Phytoremediation of soil contaminated with low concentrations of radionuclides. *Water Air Soil Pollut.* **88,** 167–176.

Fässler, E., Robinson, B. H., Stauffer, W., Gupta, S. K., Papritz, A., and Schulin, R. (2010). Phytomanagement of metal-contaminated agricultural land using sunflower, maize and tobacco. *Agric. Ecosyst. Environ.* **136,** 49–58.

Fernandez, M. D., Cagigal, E., Vega, M. M., Urzelai, A., Babin, M., Pro, J., and Tarazona, J. V. (2005). Ecological risk assessment of contaminated soils through direct toxicity assessment. *Ecotoxicol. Environ. Saf.* **62,** 174–184.
Fitz, W. J., Wenzel, W. W., Zhang, H., Nurmi, J., Stipek, K., Fischerova, Z., Schweiger, P., Kollensperger, G., Ma, L. Q., and Stingeder, G. (2003). Rhizosphere characteristics of the arsenic hyperaccumulator *Pteris vittata* L. and monitoring of phytoremoval efficiency. *Environ. Sci. Technol.* **37,** 5008–5014.
Flege, A. (2000). Forest recultivation of coal-mined land: Problems and prospects. *In* "Reclaimed Land" (M. J. Haigh, Ed.), pp. 291–337. A.A. Balkema, Rotterdam, Netherlands.
Francesconi, K., Visoottiviseth, P., Sridokchan, W., and Goessler, W. (2002). Arsenic species in an arsenic hyperaccumulating fern, *Pityrogramma calomelanos*: A potential phytoremediator of arsenic-contaminated soils. *Sci. Total Environ.* **284,** 27–35.
Frankenberger, W. T., and Losi, M. E. (1995). Application of bioremediation in the cleanup of heavy elements and metalloids. *In* "Bioremediation: Science and Applications" (H. D. Skipper and R. F. Turco, Eds.), Soil Science Special Publication No. 43, pp. 173–210. Soil Science Society of America, Madison, WI.
Freitas, H., Prasad, M. N. V., and Pratas, J. (2004). Plant community tolerant to trace elements growing on the degraded soils of Sao Domingos mine in the south east of Portugal: Environmental implications. *Environ. Int.* **30,** 65–72.
Gadd, G. M. (1992). Microbial control of heavy metal pollution. *In* "Microbial Control of Pollution" (J. C. Fry, G. M. Gadd, R. A. Herbert, C. W. Jones, and I. A. Watson-Craik, Eds.), pp. 69–88. Society for General Microbiology, Great Britain.
Gao, Y., Miao, C., Mao, L., Zhou, P., Jin, Z., and Shi, W. (2010). Improvement of phytoextraction and antioxidative defense in *Solanum nigrum* L. under cadmium stress by application of cadmium-resistant strain and citric acid. *J. Hazard. Mater.* **181,** 771–777.
Garten, C. T. Jr. (1999). Modeling the potential role of a forest ecosystem in phytostabilization and phytoextraction of 90Sr at a contaminated watershed. *J. Environ. Radioact.* **43,** 305–323.
Gatliff, E. G. (1994). Vegetative remediation process offers advantages over traditional pump-and-treat technologies. *Remed. J.* **4,** 343–352.
Glick, B. R., and Bashan, Y. (1997). Genetic manipulation of plant growth-promoting bacteria to enhanced biocontrol of phytopathogens. *Biotechnol. Adv.* **15,** 353–378.
Glick, B. R., Penrose, D. M., and Li, J. (1998). A model for the lowering of plant ethylene concentrations by plant growth-promoting bacteria. *J. Therm. Biol.* **190,** 63–68.
Gonzaga, M. I. S., Santos, J. A. G., and Ma, L. Q. (2006). Arsenic chemistry in the rhizosphere of *Pteris vittata* L. and *Nephrolepis exaltata* L. *Environ. Pollut.* **143,** 254–260.
Granel, T., Robinson, B., Mills, T., Clothier, B., Green, S., and Fung, L. (2002). Cadmium accumulation by willow clones used for soil conservation, stock fodder, and phytoremediation. *Aust. J. Soil Res.* **40,** 1331–1337.
Gray, C. W., Dunham, S. J., Dennis, P. G., Zhao, F. J., and McGrath, S. P. (2006). Field evaluation of in situ remediation of a heavy metal contaminated soil using lime and red-mud. *Environ. Pollut.* **142,** 530–539.
Grayston, S. J., Vaughan, D., and Jones, D. (1997). Rhizosphere carbon flow in trees, in comparison with annual plants: The importance of root exudation and its impact on microbial activity and nutrient availability. *Appl. Soil Ecol.* **5,** 29–56.
Grifferty, A., and Barrington, S. (2000). Zinc uptake by young wheat plants under two transpiration regimes. *J. Environ. Qual.* **29,** 443–446.
Grifoll, J., and Cohen, Y. (1996). Contaminant migration in the unsaturated soil zone: The effect of rainfall and evapotranspiration. *J. Contam. Hydrol.* **23,** 185–211.
Gworek, B. (1992). Inactivation of cadmium in contaminated soils using synthetic zeolites. *Environ. Pollut.* **75,** 269–271.

Hadi, F., Bano, A., and Fuller, M. P. (2010). The improved phytoextraction of lead (Pb) and the growth of maize (*Zea mays* L.): The role of plant growth regulators (GA3 and IAA) and EDTA alone and in combinations. *Chemosphere* **80,** 457–462.

Hall, J. L. (2002). Cellular mechanisms for heavy metal detoxification and tolerance. *J. Exp. Bot.* **53,** 1–11.

Hall, J. A., Peirson, D., Ghosh, S., and Glick, B. R. (1996). Root elongation in various agronomic crops by the plant growth promoting rhizobacterium *Pseudomonas putida* GR12-2. *Isr. J. Plant Sci.* **44,** 37–42.

Harris, J. N., New, P. B., and Martin, P. M. (2006). Laboratory tests can predict beneficial effects of phosphate-solubilising bacteria on plants. *Soil Biol. Biochem.* **38,** 1521–1526.

Haselwandter, K., and Bowen, G. (1996). Mycorrhizal relations in trees for agroforestry and land rehabilitation. *Forest. Ecol. Manage.* **81,** 1–17.

He, Y. K., Sun, J. G., Feng, X. Z., Czako, M., and Marton, L. (2001). Differential mercury volatilization by tobacco organs expressing a modified bacterial merA gene. *Cell Res.* **11,** 231–236.

He, Z. L., Yang, X. E., and Stoffella, P. J. (2005). Trace elements in agroecosystems and impacts on the environment. *J. Trace Elem. Med. Biol.* **19,** 125–140.

Hesterberg, D., Bril, J., and del Castilho, P. (1993). Thermodynamic modeling of zinc, cadmium, and copper solubility in manure, acidic loamy-sand topsoil. *J. Environ. Qual.* **22,** 681–1993.

Hetherington, A. M., and Woodward, F. I. (2003). The role of stomata in sensing and driving environmental change. *Nature* **424,** 901–908.

Hetrick, B. A. D., Wilson, G. W. T., and Figge, D. A. H. (1994). The influence of mycorrhizal symbiosis and fertilizer amendments on establishment of vegetation in heavy metal mine spoil. *Environ. Pollut.* **86,** 171–179.

Higgins, T. E., Halloran, A. R., Dobbins, M. E., and Pittignano, A. J. (1998). In situ reduction of hexavalent chromium in alkaline soils enriched with chromites ore processing residue. *J. Air Waste Manage. Assoc.* **48,** 100–1106.

Hinsinger, P. (2001). Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: A review. *Plant Soil* **237,** 173–195.

Hinsinger, P., Gobran, G. R., Gregory, P. J., and Wenzel, W. W. (2005). Rhizosphere geometry and heterogeneity arising from root-mediated physical and chemical processes. *New Phytol.* **168,** 293–303.

Honda, M., Tamura, H., Kimura, T., Kinoshita, T., Mastsufuru, H., and Sasto, T. (2007). Control of lead polluted leachate in a box-scale phytoremediation test using common buckwheat (*Fagopyrum esculentum* Moench) grown on lead contaminated soil. *Environ. Technol.* **28,** 425–431, http://www.tenby10.com/Index.

Huang, P. M. (2004). Soil mineral-organic matter-microorganism interactions: Fundamentals and impacts. *Adv. Agron.* **82,** 391–472.

Hupy, J. P. (2004). Influence of vegetation cover and crust type on wind-blown sediment in a semi-arid climate. *J. Arid Environ.* **58,** 167–179.

Jardine, P. M., Fendorf, S. E., Mayes, M. A., Larsen, I. L., Brooks, S. C., and Bailey, W. B. (1999). Fate and transport of hexavalent chromium in undisturbed heterogeneous soil. *Environ. Sci. Technol.* **33,** 2939–2944.

Jentschke, G., and Godbold, D. L. (2000). Metal toxicity and ectomycorrhizas. *Physiol. Plant.* **109,** 107–116.

Jones, D. L., Hodge, A., and Kuzyakov, Y. (2004). Plant and mycorrhizal regulation of rhizodeposition. *New Phytol.* **163,** 459–480.

Kamensky, M., Ovadis, M., Chet, I., and Chernin, L. (2003). Soil-borne strain IC14 of *Serratia plymuthica* with multiple mechanisms of antifungal activity provides biocontrol of *Botrytis cinerea* and *Sclerotinia sclerotiorum* diseases. *Soil Biol. Biochem.* **35,** 323–331.

Kanazawa, S., Asakawa, S., and Takai, S. (1988). Effect of fertilizer and manure application on microbial numbers, biomass, and enzyme activities in volcanic ash soils. 1. Microbial numbers and biomass carbon. *Soil Sci. Plant Nutri.* **34,** 429–439.

Keller, C., Marchetti, M., Rossi, L., and Lugon-Moulin, N. (2005). Reduction of cadmium availability to tobacco (*Nicotiana tabacum*) plants using soil amendments in low cadmium-contaminated agricultural soils: A pot experiment. *Plant Soil* **276,** 69–84.

Khattak, R. A., Page, A. L., Parker, D. R., and Bakhtar, D. (1991). Accumulation and interactions of arsenic, selenium, molybdenum and phosphorous in alfalfa. *J. Environ. Qual.* **20,** 165–168.

Kim, S., Lim, H., and Lee, I. (2010). Enhanced heavy metal phytoextraction by *Echinochloa crus-galli* using root exudates. *J. Biosci. Bioeng.* **109,** 47–50.

Kline, A. B. (2008). Hydraulic Control in Willow Phytoremediation Systems at Fort Drum. State University of New York College of Environmental Science and Forestry, New York, M.Sc. thesis.

Ko, B. G., Anderson, C. W. N., Bolan, N. S., Huh, K. Y., and Vogeler, I. (2008). Potential for the phytoremediation of arsenic-contaminated mine tailings in Fiji. *Aust. J. Soil Res.* **46,** 493–501.

Koerner, G. R., and Koerner, R. M. (2006). Geotextile tube assessment using a hanging bag test. *Geotex. Geomembr.* **24,** 129–137.

Kumpiene, J., Lagerkvist, A., and Maurice, C. (2007). Stabilization of As, Cr, Cu, Pb and Zn in soils using amendments—A review. *Waste Manage.* **28,** 215–225.

Kutay, M. E., and Aydilek, A. H. (2004). Retention performance of geotextile containers confining geomaterials. *Geosynth. Int.* **11,** 100–113.

Kutay, M. E., and Aydilek, A. H. (2005). Filtration performance of two-layer geotextile systems. *Geotech. Test. J.* **28,** 79–91.

Lan, C. Y., Shu, W. S., and Wong, M. H. (1997). Revegetation of lead/zinc mine tailings at Shaoguan, Guandong province, China: Phytotoxicity of the tailings. *Stud. Environ. Sci.* **66,** 119–130.

Lange, K., Rowe, R. K., and Jamieson, H. (2007). The potential role of geosynthetic clay liners in mine water treatment systems. *Geotext. Geomembr.* **28,** 199–205.

Legrand, P., Turmel, M. C., Sauvé, S., and Courchesne, F. (2005). Speciation and bioavailability of trace metals (Cd, Cu, Ni, Pb, Zn) in the rhizosphere of contaminated soils. *In* "Biogeochemistry of Trace Elements in the Rhizosphere" (P. M. Huang and G. R. Gobran, Eds.), pp. 261–299. Elsevier, New York.

Leung, H. M., Wu, F. Y., Cheung, K. C., Ye, Z. H., and Wong, M. H. (2010). The effect of arbuscular mycorrhizal fungi and phosphate amendment on arsenic uptake, accumulation and growth of pteris vittata in As-contaminated soil. *Int. J. Phytoremediation* **12,** 384–403.

Liao, Y. C., Chien, S. W. C., Wang, M. C., Shen, Y., Hung, P. L., and Das, B. (2006). Effect of transpiration on Pb uptake by lettuce and on water soluble low molecular weight organic acids in rhizosphere. *Chemosphere* **65,** 343–351.

Lifshitz, R., Kloepper, J. W., Kozlowski, M., Simonson, C., Carlson, J., Tipping, E. M., and Zaleska, I. (1987). Growth promotion of canola (rapeseed) seedlings by a strain of *Pseudomonas putida* under gnotobiotic conditions. *Can. J. Microbiol.* **33,** 390–395.

Liu, J., Liang, J., Li, K., Zhang, Z., Yu, B., Lu, X., Yang, J., and Zhu, Q. (2003). Correlations between cadmium and mineral nutrients in absorption and accumulation in various genotypes of rice under cadmium stress. *Chemosphere* **52,** 1467–1473.

Liu, D., Islam, E., Li, T., Yang, X., Jin, X., and Mahmood, Q. (2008). Comparison of synthetic chelators and low molecular weight organic acids in enhancing phytoextraction of heavy metals by two ecotypes of *Sedum alfredii* Hance. *J. Hazard. Mater.* **153,** 114–122.

Liu, X., Peng, K., Wang, A., Lian, C., and Shen, Z. (2010). Cadmium accumulation and distribution in populations of *Phytolacca americana* L. and the role of transpiration. *Chemosphere* **78,** 1136–1141.

Loch, R. J. (2000). Effects of vegetation cover on runoff and erosion under simulated rain and overland flow on a rehabilitated site on the Meandu mine, Tarong, Queensland. *Aust. J. Soil Res.* **38,** 299–312.
Lock, K., and Janssen, C. R. (2003). Influence of aging on metal availability in soils. *Rev. Environ. Contam. Toxicol.* **179,** 1–21.
López, M. L., Peralta-Videa, J. R., Benitez, T., and Gardea-Torresdey, J. L. (2005). Enhancement of lead uptake by alfalfa (*Medicago sativa*) using EDTA and a plant growth promoter. *Chemosphere* **61,** 595–598.
Losi, M. E., Amrhein, C., and Frankenberger, W. T. (1994). Factors affecting chemical and biological reduction of Cr(VI)in soil. *Environ. Toxicol. Chem.* **13,** 1727–1735.
Lothenbach, B., Furrer, G., Schärli, H., and Schulin, R. (1999). Immobilization of zinc and cadmium by montmorillonite compounds: Effects of aging and subsequent acidification. *Environ. Sci. Technol.* **33,** 2945–2952.
Lu, L., Tian, S., Yang, X., Li, T., and He, Z. (2009). Cadmium uptake and xylem loading are active processes in the hyperaccumulator *Sedum alfredii*. *J. Plant Physiol.* **166,** 579–587.
Lynch, J. M., and Whipps, J. M. (1990). Substrate flow in the rhizosphere. *Plant Soil* **129,** 1–10.
Lytle, C. M., Lytle, F. W., Yang, N., Qian, J. H., Hansen, D., Zayed, A., and Terry, N. (1998). Reduction of Cr (VI) to Cr (III) by wetland plants: Potential for in situ heavy metal detoxification. *Environ. Sci. Technol.* **32,** 3087–3093.
Ma, L. Q., Komar, K. M., Tu, C., Zhang, W. H., Cai, Y., and Kennelley, E. D. (2001). A fern that hyperaccumulates arsenic—A hardy, versatile, fast-growing plant helps to remove arsenic from contaminated soils. *Nature* **409,** 579.
Mantelin, S., and Touraine, B. (2004). Plant growth-promoting bacteria and nitrate availability: Impacts on root development and nitrate uptake. *J. Exp. Bot.* **55,** 27–34.
Mapa, R. B. (1995). Effect of reforestation using *Tectona grandis* on infiltration and soil water retention. *For. Ecol. Manage.* **77,** 119–125.
Marchiol, L., Assolari, S., Sacco, P., and Zerbi, G. (2004). Phytoextraction of heavy metals by canola (*Brassica napus*) and radish (*Raphanus sativus*) grown on multicontaminated soil. *Environ. Pollut.* **132,** 21–27.
María, I. S., Nora, F., and Atilio, J. B. (2002). The effect of inoculation with *Azospirillum brasilense* on growth and nitrogen utilization by wheat plants. *Plant Soil* **245,** 215–222.
Marschner, P., Yang, C. H., Lieberei, R., and Crowley, D. E. (2001). Soil and plant specific effects on bacterial community composition in the rhizosphere. *Soil Biol. Biochem.* **33,** 1437–1445.
Martínez-Alcalá, I., Walker, D. J., and Bernal, M. P. (2010). Chemical and biological properties in the rhizosphere of *Lupinus albus* alter soil heavy metal fractionation. *Ecotoxicol. Environ. Saf.* **73,** 595–602.
McCallum, M. H., Kirkegaard, J. A., Green, T. W., Cresswell, H. P., Davies, S. L., Angus, J. F., and Peoples, M. B. (2004). Improved subsoil macroporosity following perennial pastures. *Aust. J. Exp. Agric.* **44,** 299–307.
McGowen, S. L., Basta, N. T., and Brown, G. O. (2001). Use of diammonium phosphate to reduce heavy metal solubility and transport in smelter-contaminated soil. *J. Environ. Qual.* **30,** 493–500.
McGrath, S. P., and Zhao, F. (2003). Phytoextraction of metals and metalloids from contaminated soils. *Curr. Opin. Biotechnol.* **14,** 277–282.
McGrath, S. P., Zhao, F. J., and Lombi, E. (2001). Plant and rhizosphere processes involved in phytoremediation of metal-contaminated soils. *Plant Soil* **232,** 207–214.
McGrath, S. P., Zhao, F. J., and Lombi, E. (2002). Phytoremediation of metals, metalloids, and radionuclides. *Adv. Agron.* **75,** 1–56.
McLaughlin, M. J., Hamon, R. E., McLaren, R. G., Speir, T. W., and Rogers, S. L. (2000). Review: A bioavailability-based rationale for controlling metal and metalloid

contamination of agricultural land in Australia and New Zealand. *Aust. J. Soil Res.* **38,** 1037–1086.
Meers, E., Ruttens, A., Hopgood, M., Lesage, E., and Tack, F. M. G. (2005). Potential of *Brassic rapa*, *Cannabis sativa*, *Helianthus annuus* and *Zea mays* for phytoextraction of heavy metals from calcareous dredged sediment derived soils. *Chemosphere* **61,** 561–572.
Meier, S., Borie, F., Bolan, N., and Cornejo, P. (2011). Remediation of metal polluted soils by arbuscular mycorrhizal fungi. *Crit. Rev. Environ. Sci. Technol.*(accepted for publication).
Mench, M., and Martin, E. (1991). Mobilization of cadmium and other metals from 2 soils by root exudates of zea-mays L., nicotiana-tabacum L. and nicotiana rustica L.. *Plant Soil* **132,** 187–196.
Mench, M. J., Didier, V. L., Loffler, M., Gomez, A., and Masson, P. (1994). A mimicked in-situ remediation study of metal-contaminated soils with emphasis on cadmium and lead. *J. Environ. Qual.* **23,** 58–63.
Mendez, M. O., and Maier, R. M. (2008). Phytostabilization of mine tailings in arid and semiarid environments-an emerging remediation technology. *Environ. Health Perspect.* **116,** 278.
Menzie, C., Burke, A. M., Grasso, D., Harnois, M., Magee, B., McDonald, D., Montgomery, C., Nichols, A., Pignatello, J., Price, B., Price, R., Rose, J., *et al.* (2000). An approach for incorporating information on chemical availability in soils into risk assessment and risk-based decision making. *Hum. Ecol. Risk Assess.* **6,** 479–510.
Meyer, J., Schmidt, A., Michalke, K., and Hensel, R. (2007). Volatilisation of metals and metalloids by the microbial population of an alluvial soil. *Syst. Appl. Microbiol.* **30,** 229–238.
Miller, J. R., and Miller, S. M. O. (2007). Contaminated Rivers. Springer, Dordrecht.
Mohammad, A. G., and Adam, M. A. (2010). The impact of vegetative cover type on runoff and soil erosion under different land uses. *Catena* **81,** 97–103.
Moo-Young, H., and Tucker, W. R. (2002). Evaluation of vacuum filtration testing for geotextile tubes. *Geotext. Geomembr.* **20,** 191–212.
Moreno, F. N., Anderson, C. W. N., Stewart, R. B., and Robinson, B. H. (2005). Mercury volatilisation and phytoextraction from base-metal mine tailings. *Environ. Pollut.* **136,** 341–352.
Morgan, J. A. W., Bending, G. D., and White, P. J. (2005). Biological costs and benefits to plant–microbe interactions in the rhizosphere. *J. Exp. Bot.* **56,** 1729.
Morrell, J., Stewart, R. B., Gregg, P. E. H., Bolan, N. S., and Horne, D. (1996). An assessment of sulphide oxidation in abandoned base-metal tailings, Te Aroha, New Zealand. *Environ. Pollut.* **94,** 217–225.
Mott, C. J. B. (1981). Anion and ligand exchange. *In* "The Chemistry of Soil Processes" (D. J. Greenland and M. H. B. Haynes, Eds.), pp. 179–219. John Wiley & Sons, New York.
Murakami, M., and Ae, N. (2009). Potential for phytoextraction of copper, lead, and zinc by rice (*Oryza sativa* L.), soybean (*Glycine max* [L.] Merr.), and maize (*Zea mays* L.). *J. Hazard. Mater.* **162,** 1185–1192.
Naidu, R., Bolan, N. S., Kookona, R., and Tiller, K. (1994). Effect of ionic strength on the adsorption of cadmium by soils. *Eur. J. Soil Sci.* **45,** 419–430.
Naidu, R., Kookana, R. S., Sumner, M. E., Harter, R. D., and Tiller, K. G. (1996). Cadmium adsorption and transport in variable charge soils: A review. *J. Environ. Qual.* **26,** 602–617.
Naidu, R., Semple, K. T., Megharaj, M., Juhasz, A. L., Bolan, N. S., Gupta, S., Clothier, B., Schulin, R., and Chaney, R. (2008a). Bioavailability, definition, assessment and implications for risk assessment. *In* "Chemical Bioavailability in Terrestrial Environment" (R. Naidu, Ed.), pp. 39–52. Elsevier, Amsterdam.

Naidu, R., Pollard, S. J. T., Bolan, N. S., Owens, G., and Pruszinski, A. W. (2008b). Bioavailability: The underlying basis for risk based land management. *In* "Chemical Bioavailability in Terrestrial Environment" (R. Naidu, Ed.), pp. 53–72. Elsevier, Amsterdam.

Nedjimi, B., and Daoud, Y. (2009). Cadmium accumulation in Atriplex halimus subsp. schweinfurthii and its influence on growth, proline, root hydraulic conductivity and nutrient uptake. *Flora-Morphol. Distribution. Funct. Ecol. Plant.* **204,** 316–324.

Neng-Chang, C., and Huai-Man, C. (1992). Chemical behavior of cadmium in wheat rhizosphere. *Pedosphere* **2,** 363–371.

Neunhauserer, C., Berreck, M., and Insam, H. (2001). Remediation of soils contaminated with molybdenum using soil amendments and phytoremediation. *Water Air Soil Pollut.* **128,** 85–96.

Norland, M. R., and Veith, D. L. (1995). Revegetation of coarse taconite iron ore tailing using municipal solid waste compost. *J. Hazard. Mater.* **41,** 123–134.

NRC. National Research Council. (2003). Bioavailability of Contaminants in Soils and Sediments. Academy Press, Washington.

Nyer, E. K., and Gatliff, E. G. (1996). Phytoremediation. *Ground Water Monit. Rem.* **16,** 58–62.

Okon, Y., and Vanderleyden, J. (1997). Root-associated Azospirillum species can stimulate plants. *ASM News* **63,** 366–370.

Olsta, J. T., Hornaday, C. J., and Darlington, J. W. (2006). Reactive material options for in situ capping. *In* "Contaminated Sediments: Evaluation and Remediation Techniques" (M. Fukue, K. Kita, M. Ohtsubo, R. Chaney, M. Fukue, K. Kita, M. Ohtsubo, and R. Chaney, Eds.), pp. 248–253. American Society for Testing and Materials Special, Technical Publication, West Conshohocken.

Ouyang, Y. (2002). Phytoremediation: Modeling plant uptake and contaminant transport in the soil-plant-atmosphere continuum. *J. Hydrol.* **266,** 66–82.

Park, J. H., and Shin, W. S. (2006). Immobilization of Pb contaminated soil using modified clay. *Water Pract. Technol.* **1,** 1–10.

Park, J. H., Panneerselvam, P., Lamb, D., Choppala, G., and Bolan, N. S. (2011a). Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils. *J. Hazard. Mater.* **185,** 549–574.

Park, J. H., Bolan, N. S., Mallavarapu, M., and Naidu, R. (2011b). Comparative value of phosphate sources on the immobilization of lead, and leaching of lead and phosphorus in lead contaminated soils. *Sci. Total Environ.* **409,** 853–860.

Paterson, E. (2003). Importance of rhizodeposition in the coupling of plant and microbial productivity. *Eur. J. Soil Sci.* **54,** 741–750.

Patten, C. L., and Glick, B. R. (1996). Bacterial biosynthesis of indole-3-acetic acid. *Can. J. Microbiol.* **42,** 207–220.

Patten, C. L., and Glick, B. R. (2002). Role of *Pseudomonas putida* indoleacetic acid in development of the host plant root system. *Appl. Environ. Microbiol.* **68,** 3795–3801.

Peijnenburg, W. J. G. M., Zablotskaja, M., and Vijver, M. G. (2007). Monitoring metals in terrestrial environments within a bioavailability framework and a focus on soil extraction. *Ecotoxicol. Environ. Saf.* **67,** 163–179.

Penrose, D. M., Moffatt, B. A., and Glick, B. R. (2001). Determination of 1-aminocycopropane-1-carboxylic acid (ACC) to assess the effects of ACC deaminase-containing bacteria on roots of canola seedlings. *Can. J. Microbiol.* **47,** 77–80.

Peryea, F. J. (1991). Phosphate-induced release of arsenic from soils contaminated with lead arsenate. *Soil Sci. Soc. Am. J.* **55,** 1301–1306.

Peryea, F. J., and Kammereck, R. (1997). Phosphate-enhanced movement of arsenic out of lead arsenate-contaminated topsoil and through uncontaminated subsoil. *Water Air Soil Pollut.* **93,** 243–254.

Poerschmann, J., and Kopinke, F. D. (2001). Sorption of very hydrophobic organic compounds (VHOCs) on dissolved humic organic matter (DOM). 2. Measurement of sorption and application of a Flory-Huggins concept to interpret the data. *Environ. Sci. Technol.* **35,** 1142–1148.

Pulford, I. D., and Watson, C. (2003). Phytoremediation of heavy metal-contaminated land by trees—A review. *Environ. Int.* **29,** 529–540.

Pulford, I. D., Watson, C., and McGregor, S. D. (2001). Uptake of chromium by trees: Prospects for phytoremediation. *Environ. Geochem. Health* **23,** 307–311.

Quartacci, M. F., Argilla, A., Baker, A. J. M., and Navari-Izzo, F. (2006). Phytoextraction of metals from a multiply contaminated soil by Indian mustard. *Chemosphere* **63,** 918–925.

Quartacci, M. F., Irtelli, B., Gonnelli, C., Gabbrielli, R., and Navari-Izzo, F. (2009). Naturally-assisted metal phytoextraction by *Brassica carinata*: Role of root exudates. *Environ. Pollut.* **157,** 2697–2703.

Rajkumar, M., Nagendran, R., Lee, K. J., Lee, W. H., and Kim, S. Z. (2006). Influence of plant growth promoting bacteria and Cr^{6+} on the growth of Indian mustard. *Chemosphere* **62,** 741–748.

Rasse, D. P., Rumpel, C., and Dignac, M. F. (2005). Is soil carbon mostly root carbon? Mechanisms for a specific stabilisation. *Plant Soil* **269,** 341–356.

Reid, R., and Hayes, J. (2003). Mechanisms and control of nutrient uptake in plants. *Int. Rev. Cytol.* **229,** 73–114.

Rizzi, L., Petruzzelli, G., Poggio, G., and Guidi, G. V. (2004). Soil physical changes and plant availability of Zn and Pb in a treatability test of phytostabilization. *Chemosphere* **57,** 1039–1046.

Robinson, B., and Anderson, C. (2007). Phytoremediation in New Zealand and Australia. *Phytoremediation* **23,** 455–468.

Robinson, B. H., Green, S. R., Mills, T. M., Clothier, B. E., van der Velde, M., Laplane, R., Fung, L., Deurer, M., Hurst, S., Thayalakumaran, T., and van den Dijssel, C. (2003). Phytoremediation: Using plants as biopumps to improve degraded environments. *Aust. J. Soil Res.* **41,** 599–611.

Robinson, B., Schulin, R., Nowack, B., Roulier, S., Menon, M., Clothier, B., Green, S., and Mills, T. (2006). Phytoremediation for the management of metal flux in contaminated sites. *For. Snow Landsc. Res.* **80,** 221–234.

Robinson, B. H., Green, S. R., Chancerel, B., Mills, T. M., and Clothier, B. E. (2007). Poplar for the phytomanagement of boron contaminated sites. *Environ. Pollut.* **150,** 225–233.

Robinson, B. H., Banuelos, G., Conesa, H. M., Evangelou, M. W. H., and Schulin, R. (2009). The phytomanagement of trace elements in soil. *Crit. Rev. Plant Sci.* **28,** 240–266.

Rogers, R. D., and Williams, S. E. (1986). Vesicular arbuscular mycorrhiza—Influence on plant uptake of cesium and cobalt. *Soil Biol. Biochem.* **18,** 371–376.

Romheld, V. (1991). The role of phytosiderophopes in acquisiderophores in acquisition of iron and other micronutrients in gramineous soecies—Aneciligical approach. *Plant Soil* **130,** 127–134.

Rugh, C. L., Gragson, G. M., and Meagher, R. B. (1998). Toxic mercury reduction and remediation using transgenic plants with a modified bacterial gene. *HortScience* **33,** 618–621.

Ruttens, A., Mench, M., Colpaert, J. V., Boisson, J., Carleer, R., and Vangronsveld, J. (2006). Phytostabilization of a metal contaminated sandy soil. I: Influence of compost and/or inorganic metal immobilizing soil amendments on phytotoxicity and plant availability of metals. *Environ. Pollut.* **144,** 524–532.

Sabti, H., Hossain, M., Brooks, R., and Stewart, R. (2000). The current environmental impact of base metal mining at the Tui Mine, Te Aroha, New Zealand. *J. R. Soc. N. Z.* **30,** 197–208.

Saha, S., Mina, B. L., Gopinath, K. A., Kundu, S., and Gupta, H. S. (2008). Organic amendments affect biochemical properties of a subtemperate soil of the Indian Himalayas. *Nutr. Cycl. Agroecosyst.* **80,** 233–242.

Sajjad, M., Waseem, A., Farooq, L., Jacqueline, H., Rene, B., Philippe, N., and Kauser, A. M. (2004). Isolation, partial characterization, and the effect of plant growth-promoting bacteria (PGPB) on micro-propagated sugarcane in vitro. *Plant Soil* **237,** 47–54.

Salah, S. A., and Barrington, S. F. (2006). Effect of soil fertility and transpiration rate on young wheat plants (*Triticum aestivum*) Cd/Zn uptake and yield. *Agric. Water Manage.* **82,** 177–192.

Salt, D. E., Smith, R. D., and Raskin, I. (1998). Phytoremediation. *Annu. Rev. Plant Phys.* **49,** 643–668.

Sander, M. L., and Ericsson, T. (1998). Vertical distributions of plant nutrients and heavy metals in Salix viminalis stems and their implications for sampling. *Biomass Bioenergy* **14,** 57–66.

Satpute, S. K., Banat, I. M., Dhakephalkar, P. K., Banpurkar, A. G., and Chopade, B. A. (2010). Biosurfactants, bioemulsifiers and exopolysaccharides from marine microorganisms. *Biotechnol. Adv.* **28,** 436–450.

Schiewer, S., and Volesky, B. (1995). Modeling of the proton-metal ion-exchange in biosorption. *Environ. Sci. Technol.* **29,** 3049–3058.

Schnoor, J. L., Licht, L. A., McCutcheon, S. C., Wolfe, N. L., and Carreira, L. H. (1995). Phytoremediation of organic and nutrient contaminants. *Environ. Sci. Technol.* **29,** A318–A323.

Schutzendubel, A., and Polle, A. (2002). Plant responses to abiotic stresses: Heavy metal-induced oxidative stress and protection by mycorrhization. *J. Exp. Bot.* **53,** 1351–1365.

Sessitsch, A., and Puschenreiter, M. (2008). Endophytes and rhizosphere bacteria of plants growing in heavy metal-containing soils. *In* "Microbiology of Extreme Soils" (P. Dion and C. S. Nautiyal, Eds.), 978-3-540-74230-2, pp. 317–332. Springer, Berlin Heidelberg.

Sharma, A., and Johri, B. N. (2003). Growth promoting influence of siderophore-producing *Pseudomonas* strains GRP3A and PRS_9 in maize (*Zea mays* L.) under iron limiting conditions. *Microbiol. Res.* **158,** 243–248.

Sheng, X., and Xia, J. (2006). Improvement of rape (*Brassica napus*) plant growth and cadmium uptake by cadmium-resistant bacteria. *Chemosphere* **64,** 1036–1042.

Shenker, M., Fan, T. W. M., and Crowley, D. E. (2001). Phytosiderophores influence on cadmium mobilization and uptake by wheat and barley plants. *J. Environ. Qual.* **30,** 2091–2098.

Simon, A., and Collison, A. J. C. (2002). Quantifying the mechanical and hydrologic effects of riparian vegetation on streambank stability. *Earth Surf. Process. Landforms* **27,** 527–546.

Skulsky, I. A. (1991). Isomorphism of Tl^+ and K^+ in membrane-transport processes. *Tsitologiya* **33,** 118–129.

Smith, E., Naidu, R., and Alston, A. M. (1999). Chemistry of arsenic in soils: I sorption of arsenate and arsenite by four Australian soils. *J. Environ. Qual.* **28,** 1719–1726.

Spark, D. L. (1986). Soil Physical Chemistry. CRC Press, Boca Raton, FL.

Sposito, G. (1984). The Surface Chemistry of Soils. Oxford University Press, New York.

Stokes, J. D., Paton, G. I., and Semple, K. T. (2005). Behaviour and assessment of bioavailability of organic contaminants in soil: Relevance for risk assessment and remediation. *Soil Use Manage.* **24,** 475–486.

Stomp, A. M., Han, K. H., Wilbert, S., and Gordon, M. P. (1993). Genetic-improvement of tree species for remediation of hazardous wastes. *In Vitro Cell. Dev. Biol. Plant* **29,** 227–232.

Sundara, B., Natarajan, V., and Hari, K. (2002). Influence of phosphorus solubilizing bacteria on the changes in soil available phosphorus and sugarcane and sugar yields. *Field Crop. Res.* **77,** 43–49.

Swartjes, F. A. (1999). Risk-based assessment of soil and groundwater quality in the Netherlands: Standards and remediation urgency. *Risk Anal.* **19,** 1235–1249.

Tack, F. M., Callewaert, O. W. J. J., and Verloo, M. G. (1996). Metal solubility as a function of pH in a contaminated, dredged sediment affected by oxidation. *Environ. Pollut.* **91,** 199–208.

Tang, C., and Rengel, Z. (2003). Role of plant cation/anion uptake ratio in soil acidification. *In* "Handbook of Soil Acidity" (Z. Rengel, Ed.), pp. 57–81. Marcel Dekker, New York.

Tani, F. H., and Barrington, S. (2005). Zinc and copper uptake by plants under two transpiration rates. Part II. Buckwheat (*Fagopyrum esculentum* L.). *Environ. Pollut.* **138,** 548–558.

Tanimoto, E. (1987). Gibberellin-dpendent root elongation in Lactuca sativa: Recovery from growth retardant-suppressed elongation with thickening by low concentration of GA3. *Plant Cell Physiol.* **28,** 963–973.

Tejada, M. (2009). Application of different organic wastes in a soil polluted by cadmium: Effects on soil biological properties. *Geoderma* **153,** 254–268.

Tejada, M., Hernandez, M. T., and Garcia, C. (2006). Application of two organic amendments on soil restoration: Effects on the soil biological properties. *J. Environ. Qual.* **35,** 1010–1017.

Tepfer, D., Metzger, L., and Prost, R. (1989). Use of roots transformed by agrobacterium-rhizogenes in rhizosphere research—Applications in studies of candmium assimilation from sewage sludges. *Plant Mol. Biol.* **13,** 295–302.

Terry, N., Zayed, A. M., de Souza, M. P., and Tarun, A. S. (2000). Selenium in higher plants. *Annu. Rev. Plant Physiol. Plant Mol. Boil.* **51,** 401–432.

Thayalakumaran, T., Robinson, B. H., Vogeler, I., Scotter, D. R., Clothier, B. E., and Percival, H. J. (2003). Plant uptake and leaching of copper during EDTA-enhanced phytoremediation of repacked and undisturbed soil. *Plant Soil* **254,** 415–423.

Tiller, K. G. (1989). Heavy metals in soils and their environmental significance. *Adv. Soil Sci.* **9,** 113–142.

Tordoff, G. M., Baker, A. J. M., and Willis, A. J. (2000). Current approaches to the revegetation and reclamation of metalliferous mine wastes. *Chemosphere* **41,** 219–228.

Unterbrunner, R., Puschenreiter, M., Sommer, P., Wieshammer, G., Tlustos, P., Zupan, M., and Wenzel, W. W. (2007). Heavy metal accumulation in trees growing on contaminated sites in Central Europe. *Environ. Pollut.* **148,** 107–114.

USEPA (2001). Best Management Practices for Lead at Outdoor Shooting Ranges.EPA-902-B01-001.

Utmazian, M. N. D., Wieshammer, G., Vega, R., and Wenzel, W. W. (2007). Hydroponic screening for metal resistance and accumulation of cadmium and zinc in twenty clones of willows and poplars. *Environ. Pollut.* **148,** 155–165.

Van Herreweghe, S., Swennen, R., Cappuyns, V., and Vandecasteele, C. (2002). Chemical associations of heavy metals and metalloids in contaminated soils near former ore treatment plants: A differentiated approach with emphasis on pHstat-leaching. *J. Geochem. Explor.* **76,** 113–138.

Vangronsveld, J., and Cunningham, S. (1998). Introduction to the concepts. *In* "In situ Inactivation and Phytorestoration of Metal Contaminated Soils" (J. Vangronsveld and S. Cunningham, Eds.), pp. 1–15. Springer-Verlag and R.G. Landes Company, Berlin Heidelberg, Georgetown.

Vangronsveld, J., Van Assche, F., and Clijsters, H. (1995a). Reclamation of a bare industrial area contaminated by non-ferrous metals: In situ metal immobilization and revegetation. *Environ. Pollut.* **87,** 51–59.

Vangronsveld, J., Sterckx, J., Van Assche, F., and Clijsters, H. (1995b). Rehabilitation studies on an old non-ferrous waste dumping ground: Effects of revegetation and metal immobilization by beringite. *J. Geochem. Explor.* **52,** 221–229.

Vásquez-Méndez, R., Ventura-Ramos, E., Oleschko, K., Hernández-Sandoval, L., Parrot, J. F., and Nearing, M. A. (2010). Soil erosion and runoff in different vegetation patches from semiarid Central Mexico. *Catena* **80,** 162–169.

Venkatraman, K., and Ashwath, N. (2007). Phytocapping: An alternative technique for reducing leachate and methane generation from municipal landfills. *Environmentalist* **27,** 155–164.

Veselov, G., Kudoyarova, G., Symonyan, M., and Veselov, S. T. (2003). Effect of cadmium on ion uptake, transpiration and cytokinin content in wheat seedlings. *Bulg. J. Plant Physiol.*(Special Issue), 353–359.

Vig, K., Megharaj, M., Sethunathan, N., and Naidu, R. (2003). Bioavailability and toxicity of cadmium to microorganisms and their activities in soil: A review. *Adv. Environ. Res.* **8,** 121–135.

Villegas, J., and Fortin, J. A. (2002). Phosphorus solubilization and pH changes as a result of the interactions between soil bacteria and arbuscular mycorrhizal fungi on a medium containing NO_3^- as nitrogen source. *Can. J. Chem.* **80,** 571–576.

Von Wiren, N., Marschner, H., and Römheld, V. (1996). Roots of iron efficient maize also absorb phytosiderophore-chelated zinc. *Plant Physiol.* **111,** 1119–1125.

Walter, A., Romheld, V., Marschner, H., and Mori, S. (1994). Is the release of phytosiderophores in zinc—Deficient wheat plants a response to response to impaired iron utilization. *Physiol. Plant.* **92,** 493–500.

Wang, C., Knill, E., Glick, B. R., and Defago, G. (2000). Effect of transferring 1-aminocyclopropane-1-carboxylic acid (ACC) deaminase genes into *Pseudomonas fluorescens* strain CHA0 and its gacA derivative CHA96 on their growth-promoting and disease-suppressive capacities. *Can. J. Microbiol.* **46,** 898–907.

Wann, S. S., and Uehara, G. (1978). Surface charge manipulation in constant surface potential soil colloids: I. Relation to sorbed phosphorus. *Soil Sci. Soc. Am. J.* **42,** 565–570.

Wardle, D. A. (1992). A comparative assessment of factors which influence microbial biomass carbon and nitrogen levels in soil. *Biol. Rev.* **67,** 321–358.

Wei, S., Zhou, Q., and Wang, X. (2005). Identification of weed plants excluding the uptake of heavy metals. *Environ. Int.* **31,** 829–834.

Wenzel, W. W., Bunkowski, M., Puschenreiter, M., and Horak, O. (2003). Rhizosphere characteristics of indigenously growing nickel hyperaccumulator and excluder plants on serpentine soil. *Environ. Pollut.* **123,** 131–138.

Willscher, S., Hertwig, T., Frenzel, M., Felix, M., and Starke, S. (2010). Results of remediation of hard coal overburden and tailings dumps after a few decades: Insights and conclusions. *Hydrometallurgy* **104,** 506–517.

Wong, M. H. (2003). Ecological restoration of mine degraded soils, with emphasis on metal contaminated soils. *Chemosphere* **50,** 775–780.

Xu, W. H., Liu, H., Ma, Q. F., and Xiong, Z. T. (2007). Root exudates, rhizosphere Zn fractions, and Zn accumulation of ryegrass at different soil Zn levels. *Pedosphere* **17,** 389–396.

Yang, X., Feng, Y., He, Z., and Stoffella, P. J. (2005). Molecular mechanisms of heavy metal hyperaccumulation and phytoremediation. *J. Trace Elem. Med. Biol.* **18,** 339–353.

Yang, J. Y., Yang, X. E., He, Z. L., Li, T. Q., Shentu, J. L., and Stoffella, P. J. (2006). Effects of pH, organic acids, and inorganic ions on lead desorption from soils. *Environ. Pollut.* **143,** 9–15.

Youssef, R. A., and Chino, M. (1989). Root-induced changes in the rhizosphere of plants.2. distribution of heavy-metals across the rhizosphere in soil. *Plant Nutr. Soil Sci.* **35,** 609–621.

Zaccone, C., Soler-Rovira, P., Plaza, C., Cocozza, C., and Miano, T. M. (2009). Variability in As, Ca, Cr, K, Mn, Sr, and Ti concentrations among humic acids isolated from peat using NaOH, $Na_4P_2O_7$ and NaOH + $Na_4P_2O_7$ solutions. *J. Hazard. Mater.* **167,** 987–994.

Zaidi, S., Usmani, S., Singh, B. R., and Musarrat, J. (2006). Significance of *Bacillus subtilis* strain SJ-101 as a bioinoculant for concurrent plant growth promotion and nickel accumulation in Brassica juncea. *Chemosphere* **64,** 991–997.
Zayed, A. M., and Terry, N. (2003). Chromium in the environment: Factors affecting biological remediation. *Plant Soil* **249,** 139–156.
Zeng, F., Ali, S., Zhang, H., Ouyang, Y., Qiu, B., Wu, F., and Zhang, G. (2010). The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. *Environ. Pollut.* **159,** 84–91.
Zeremski-Škoric, T., Sekulic, P.Đ., Maksimovic, I. V., Šeremesic, S. I., Ninkov, J. M., Milic, S. B., and Vasin, J. R. (2010). Chelate-assisted phytoextraction: Effect of EDTA and EDDS on copper uptake by *Brassica napus* L. *J. Serb. Chem. Soc.* **75,** 1279–1289.
Zhang, F. S., Treeby, M., Romheld, V., and Marschner, H. (1991). Mobilzation of iron by phytosiderophores as affected by other micronutrients. *Plant Soil* **130,** 173–178.
Zhou, L. X., and Wong, J. W. C. (2001). Effect of dissolved organic matter from sludge and sludge compost on soil copper sorption. *J. Environ. Qual.* **30,** 878–883.
Zoysa, A. K. N., Loganathan, P., and Hedley, M. J. (1997). A technique for studying rhizosphere processes in tree crops: Soil phosphorus depletion around camellia (*Camellia japonica* L) roots. *Plant Soil* **190,** 253–265.
Zuazo, V. H. D., Martinez, J. R. F., and Raya, A. M. (2004). Impact of vegetative cover on runoff and soil erosion at hillslope scale in Lanjaron, Spain. *Environmentalist* **24,** 39–48.

CHAPTER FIVE

Synergism: A Rotation Effect of Improved Growth Efficiency

Randy L. Anderson

Contents

Abstract

Cropping systems in the Great Plains are changing because of no-till. Rotations now include a diversity of crops in contrast with rotations in tilled systems that grow only one or two crops. This diversity of crops often leads to yield increases because of the rotation effect. We have observed that crop response to the

USDA-Agricultural Research Service, Brookings, South Dakota, USA

Advances in Agronomy, Volume 112

ISSN 0065-2113, DOI: 10.1016/B978-0-12-385538-1.00005-6

rotation effect can be categorized as either improving resource-use efficiency or increasing plant size and yield capacity. An example of the efficiency response, which we term synergism, is that some crops improve water-use efficiency (WUE) of following crops. Crops produce more grain with the same water use in synergistic sequences; in contrast, crops that increase yield capacity consume more water to produce more grain. Further, synergism among crops increases tolerance of weed interference because of improved resource-use efficiency. Synergism is more prominent in low-yielding environments due to stresses such as drought, and appears to be rare among crop sequences. The cause of synergism among crops is likely related to a multitude of interacting factors such as microbial changes, growth-promoting substances, and altered nutrient cycling. Quantifying WUE as affected by preceding crop may provide a method to identify synergism among crops. No-till rotations that include synergistic crop sequences are improving land productivity, farm economics, soil health, and resource-use efficiency in the semiarid Great Plains.

1. Introduction

No-till practices have transformed crop production in the U.S. Great Plains by improving precipitation use, increasing crop yield, and restoring soil health (Peterson and Westfall, 2004). No-till has also stimulated interest in crop diversity and rotation design. Prior to no-till, rotations in the Great Plains usually consisted of one or two crops. Producers now grow four or more crops in no-till rotations (Anderson, 2005c).

After several years of no-till and crop diversity, producers noted that crop yields often exceeded expectations based on water and nutrient supply (Anderson, 2009a). Seeking to understand this change in yield, we initially attributed yield gain to the rotation effect. Crop diversity provides multiple benefits that can improve yield, such as reducing pest infestations, improving nutrient cycling, and increasing water supply (Hobbs, 2007; Vereijken, 2002). But with a long-term rotation study in the Great Plains, we observed an additional benefit of crop diversity; some crops improve water-use efficiency (WUE) of following crops (Anderson, 2009a). For example, winter wheat (*Triticum aestivum* L.) produces 10–25% more grain with the same water use following dry pea (*Pisum sativum* L.) compared with winter wheat, proso millet (*Panicum miliaceum* L.), or fallow preceding winter wheat. A similar gain in WUE was found when dry pea preceded spring wheat in the Canadian Prairies (Lafond *et al*., 2006).

As we further examined data from the Great Plains rotation study, we recognized that crop response to the rotation effect fell into two categories, either improving plant efficiency or increasing plant size, that is, capacity for yield (Anderson, 2005a). These responses differ in that yield increase with the capacity response requires more resources such as water. An example of

the capacity response is canola (*Brassica napus* L.) preceding winter wheat. Canola reduces the level of root diseases in winter wheat, enabling wheat to extract more water from soil because of healthier roots (Angus and van Herwaarden, 2001). The extra water leads to a larger plant with more capacity for yield. However, if extra soil water is not available, winter wheat yield does not increase. WUE of winter wheat does not change when canola precedes winter wheat.

A similar contrast in response to the rotation effect occurs with corn (*Zea mays* L.) and soybean (*Glycine max* Merrill). Copeland *et al.* (1993) found that soybean was more efficient in water use when grown after corn compared with continuous soybean. Conversely, corn uses more water to increase yield following soybean compared with continuous corn. Corn increases its plant size and capacity for yield when following soybean rather than improving its efficiency. Sequences that improve crop efficiency yield more with the same water use.

This change in efficiency, which we term synergism, may help producers improve crop productivity without necessarily increasing management inputs. This chapter summarizes our research to understand crop synergism and integrate this benefit into crop production systems.

2. Preceding Crop Effect on WUE

We initially observed synergism in a no-till cropping systems study in northeastern Colorado that evaluated 15 rotations (Anderson *et al.*, 1999). Rotations included crops such as corn, sunflower (*Helianthus annuus* L.), soybean, proso millet, foxtail millet (*Setaria italica* (L.) Beauv.), oat (*Avena sativa* L.), dry pea, and winter wheat. Fallow was also included in some rotations. All phases of each rotation were present in each year. We calculated WUE for grain yield based on precipitation + soil water extraction during the crop growing season. Soil water extraction to a depth of 2 m was determined for each crop with a neutron probe. Yearly rainfall averages 416 mm at this site.

2.1. Winter wheat

Five years after starting the study, WUE of winter wheat began to differ among rotations (Anderson, 2005a). Winter wheat WUE increased from 9.0 kg/ha/mm in winter wheat–fallow (W–F) to 11.2 kg/ha/mm in winter wheat–corn–fallow (W–C–F; Fig. 1). We initially speculated that WUE improved because the longer interval between winter wheat crops in W–C–F suppresses root diseases of winter wheat, as noted by Cook (1990). However, winter wheat WUE did not differ between W–F and winter wheat–proso millet–fallow (W–M–F). Further, WUE of winter

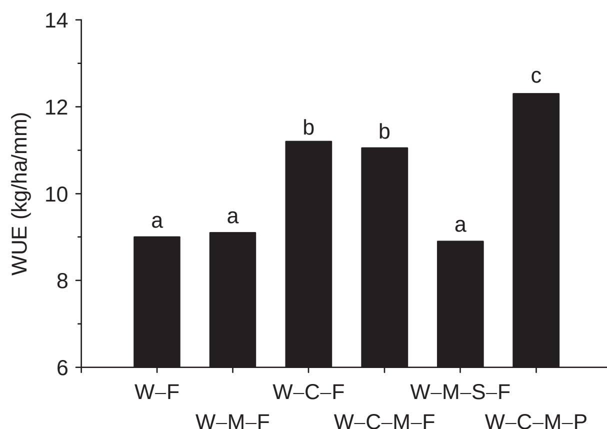


Figure 1 Water-use efficiency (WUE) of winter wheat in various no-till rotations in the Great Plains. Data collected across a 4-year interval; bars with the same letter are not significantly different based on Fischer's Protected LSD (0.05). W, winter wheat; F, fallow; C, corn; M, proso millet; S, sunflower; P, dry pea. (Adapted from Anderson, 2005a, 2009a; Anderson *et al.*, 1999.)

wheat did not increase in rotations with longer intervals between winter wheat crops; WUE of winter wheat was similar in winter wheat–corn–proso millet–fallow (W–C–M–F) and W–C–F. This change in WUE appears to be related to the presence of corn in the rotation. We also noted that dry pea, grown as a green fallow (growth terminated 7 weeks after planting), improved WUE of winter wheat in a W–C–M–P rotation. WUE of winter wheat in this rotation was 12.3 kg/ha/mm, or 11% higher than W–C–M–F or W–C–F. Compared to W–F, winter wheat produced 37% more grain in W–C–M–P with the same water use.

Winter wheat WUE did not change in any of the other rotations. For example, winter wheat WUE was the same in winter wheat–proso millet–sunflower–fallow (W–M–S–F) and W–F (Fig. 1). Only when corn and dry pea were present in the rotation did winter wheat WUE increase.

2.2. Proso millet

In this same study, we noted that proso millet WUE differed between corn and winter wheat as preceding crops. Proso millet WUE was 9.3 kg/ha/mm following corn, but only 7.5 kg/ha/mm following winter wheat (Anderson, 2005a). Total water use by proso millet was similar in both sequences, yet proso millet was 24% more efficient converting water into grain following corn. This difference in WUE was consistent across 4 years even though yields ranged from 1540 to 3510 kg/ha.

As we considered these changes in WUE with winter wheat and proso millet, we did not think that these differences could be attributed to crop management. Crops were grown with best management practices for the region (Anderson *et al.*, 1999). Fertility management was based on annual soil tests and projected yield goals, and included starter fertilizer applied with the crop seed. Weeds were effectively controlled by herbicides, and we did not observe any insect infestation that would explain the differences. We were unable to explain why this change in WUE occurred, but corn improved WUE of proso millet, whereas winter wheat WUE increased when corn and dry pea were included in the rotation. We did not observe WUE changes in other crops in the study.

2.3. Soybean

A similar change in WUE occurs when soybean follows corn. Soybean WUE increased 14% when corn preceded soybean compared to soybean following soybean (Copeland *et al.*, 1993). In contrast, corn WUE did not change when following soybean compared with continuous corn. Copeland and Crookston (1992) also quantified nutrient use in soybean and corn as affected by the rotation effect. Yield of soybean following corn increased without needing more nutrients, whereas corn following soybean used more nutrients as well as water to increase yield. Corn and soybean responded differently to the rotation effect.

3. Preceding Crop Impact on Tolerance to Weed Interference

Our data show that WUE of some crops can be improved by preceding crops. Because weeds compete with crops for water, we wondered if crop sequences improving WUE would also increase crop tolerance to weed interference. Therefore, we conducted a series of studies that evaluated preceding crop effect on winter wheat, corn, and soybean tolerance to weeds. Extensive literature has described impact of weed interference on crop yield, but seldom has research quantified the effect of preceding crops on crop tolerance to weeds.

This research was conducted in eastern South Dakota where yearly precipitation averages 580 mm. Indicator weed species were used in each crop to achieve uniform weed interference. Foxtail millet was used in corn and soybean because *Setaria* species are prominent weeds in these crops throughout the United States (Kruger *et al.*, 2009). The indicator species for winter wheat was wild rye (*Secale cereale* L.), a common weed in winter wheat (White *et al.*, 2006). In all studies, each plot was split into weed-free and weed-infested

subplots to further improve precision in assessing crop synergism. Weeds in the weed-free subplots were controlled with herbicides and hand weeding. Studies were established in fields where intensive weed management in previous years resulted in low density of the native weed community.

Crop management in all studies was based on best management practices. Nutrient management for corn and winter wheat included a starter fertilizer of N, P, and K followed by an in-crop N application during the growing season. Only starter fertilizer was applied with soybean. N fertilizer quantity was adjusted for preceding crops to include N credits for legumes. All crops were established with no-till, and the study sites had been in no-till for at least 5 years prior to starting a study.

3.1. Winter wheat

Our first study compared the impact of soybean, spring wheat, dry pea, and an oat–pea mixture (harvested for forage) on winter wheat tolerance to wild rye interference (Anderson, 2009c). We grew a short-maturity soybean that was harvested in late August, which enabled us to plant winter wheat on the same date for all treatments. Wild rye was established in winter wheat by hand planting at 15 plants/m^2, 3 days after winter wheat emergence.

Winter wheat yield varied with preceding crop in both weed-free and rye-infested conditions (Fig. 2). When wild rye was present, winter wheat yielded 4900 kg/ha following dry pea, but less than 3200 kg/ha following either soybean or spring wheat. Compared to weed-free conditions, yield loss due to wild rye was only 11% when winter wheat followed dry pea, but 32% following soybean. Even in weed-free conditions, winter wheat yielded 12% more after dry pea than following soybean. A somewhat startling trend was that winter wheat yielded as high following dry pea when wild rye was present as following soybean or spring wheat in weed-free conditions. Yield of winter wheat varied from 4000 to 6700 kg/ha during the 4 years of the study, yet impact of dry pea was consistent across years.

We included oat in one treatment to suppress root diseases in winter wheat, but the oat–pea mixture was not as favorable as dry pea alone in improving winter wheat tolerance to wild rye (Fig. 2). Yield loss due to wild rye interference when winter wheat followed oat–pea was 21%. Oat apparently interfered with the mechanism of synergism between dry pea and winter wheat, as tolerance to wild rye was less compared to winter wheat following dry pea alone.

Lower yield following spring wheat likely was due to root diseases, as legumes and oat reduce root disease severity in wheat compared to continuous wheat (Krupinsky *et al.*, 2002). But we were surprised at the difference in winter wheat yield and tolerance to weeds between dry pea and soybean as preceding crops (Fig. 2). Differences in soil water levels after harvest of the preceding crops could be one factor, but extensive precipitation occurs

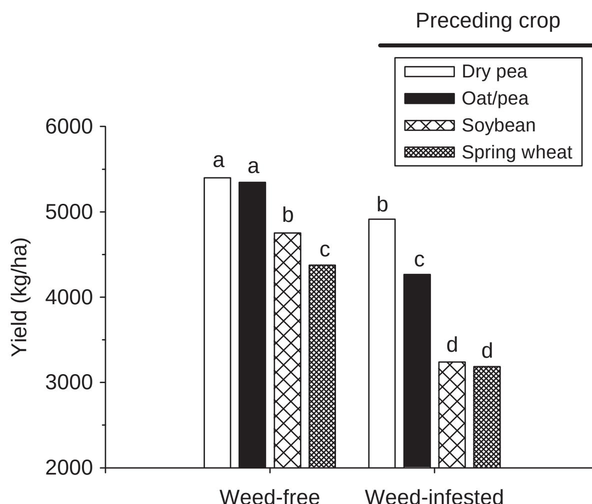


Figure 2 Winter wheat grain yield as affected by preceding crop and wild rye interference. Dry weight of wild rye at winter wheat harvest was 350 ± 23 g/m^2, averaged across all treatments. Data collected across a 4-year interval; bars with the same letter are not significantly different as determined by Fischer's Protected LSD (0.05). (Adapted from Anderson, 2009c, 2010.)

during the fall and winter at this site. Consequently, the soil profile is usually at field capacity when spring growth starts, thus eliminating differences in soil water levels among preceding crops. Another factor could be N cycling in soil differed following dry pea and soybean, but plant height of winter wheat at anthesis and wild rye biomass, measured at winter wheat harvest, did not vary due to preceding crop. Apparently, dry pea influences winter wheat growth in a unique way to reduce wild rye interference.

Spring wheat tolerance to weed interference also varies with preceding crop (Moyer *et al.*, 2004). Lentil (*Lens culinaris*, Medic) improved spring wheat tolerance to the native weed community, but mustard (*Brassica juncea* L.) and canola did not. The authors attributed this effect partially to changes in soil biology. They also noted that mustard suppressed spring wheat growth but not weeds; thus, some crop sequences may favor weed interference. Lentil may be synergistic to spring wheat, as Cayci *et al.* (2009) reported that lentil increased WUE of wheat 12% compared with fallow or other crops.

3.2. Corn

To further examine crop synergism and weed interference, we compared five crops, soybean, canola, corn, spring wheat, and dry pea, for impact on corn tolerance to foxtail millet interference (Anderson, 2007). Foxtail millet

seeds were broadcast on the soil surface the day of corn planting; ~115 seedlings/m^2 established in the corn canopy. Fresh weight of foxtail millet was measured 7 weeks after emergence and did not vary among preceding crop treatments.

Corn was most tolerant of foxtail millet following dry pea, with grain yield reduced 50% (Fig. 3). In contrast, corn following soybean, canola, or spring wheat lost almost 80% of its yield due to foxtail millet interference. Corn following corn yielded 205 kg/ha when foxtail millet was present, or only 7% of corn following dry pea. The drastic yield loss of corn following itself involves allelopathy by corn residues, which stunts seedling growth during the first 5–6 weeks of growth (Crookston, 1995). Producers who grow continuous corn in the region minimize this allelopathy by tilling to dilute the toxic compounds in soil or moving crop residues from the seed row with planter attachments (Vetsch and Randall, 2000).

Even in weed-free conditions, corn yielded more following dry pea than other crops (Fig. 3). Corn following spring wheat, soybean, or canola yielded 13% less than corn following dry pea, whereas monoculture corn yielded only 57% of corn following dry pea. An interesting trend was corn yielded similarly following dry pea with foxtail millet interference as corn following corn with weed-free conditions.

Alfalfa (*Medicago sativa* L.) and sunflower also increase corn grain yield compared to corn following corn in weed-free conditions, but Porter *et al.* (1997) found that yield gain due to these crops did not differ from soybean as a preceding crop. Dry pea appears to affect corn in a unique way to improve grain yield and tolerance to weed interference.

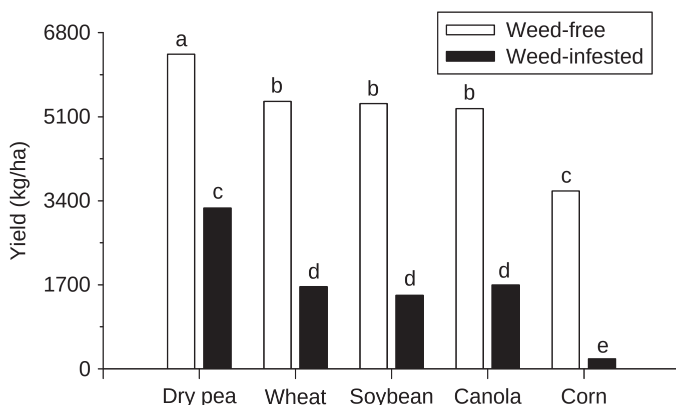


Figure 3 Corn grain yield as affected by preceding crop and foxtail millet interference. Fresh weight of foxtail millet 7 weeks after emergence was 1065 ± 85 g/m^2, averaged across all treatments. Data collected across a 4-year interval; bars with the same letter are not significantly different as determined by Fischer's Protected LSD (0.05). (Adapted from Anderson, 2007, 2008.)

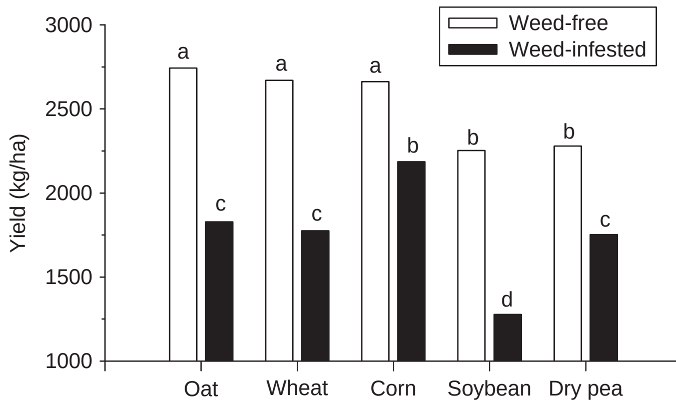


Figure 4 Soybean grain yield as affected by preceding crop and foxtail millet interference. Fresh weight of foxtail millet 7 weeks after emergence was 565 ± 51 g/m^2, averaged across all treatments. Data averaged across 2 years; bars with the same letter are not significantly different as determined by the Fischer's Protected LSD. (Adapted from Anderson, 2007, 2009a.)

3.3. Soybean

Five crops were also evaluated for impact on soybean tolerance to weeds, following the same methodology with foxtail millet used for corn (Anderson, 2009a). Soybean yield in weed-free conditions was highest following the grass crops, oat, spring wheat, and corn (Fig. 4), which may be related to suppression of root diseases in soybean (Krupinsky *et al.*, 2002). But, soybean yield was higher following corn than either oat or spring wheat when foxtail millet was present. Yield loss in soybean due to foxtail millet interference was only 18% when soybean followed corn, but more than 30% when spring wheat or oat preceded soybean. Improved tolerance to weeds when corn precedes soybean may be related to corn improving soybean WUE (Copeland *et al.*, 1993) and helping soybean tolerate weed competition for water.

Dry pea also improved soybean tolerance to foxtail millet compared to monoculture soybean, but did not improve soybean yield in weed-free conditions (Fig. 4). Dry pea apparently interacts with soybean in a different way during weed-free conditions to mask the synergistic response when foxtail millet was present.

3.4. Synergism and tolerance to weeds

Our results with crop tolerance to weeds provide further evidence of synergism; dry pea improved tolerance of winter wheat and corn to weeds, whereas corn was favorable for soybean. We were intrigued that both winter wheat and corn responded more favorably to dry pea than soybean (Figs. 2

and 3). This trend may appear to be an anomaly, but we suggest that dry pea improves WUE of winter wheat and corn and, consequently, minimizes weed interference. As noted earlier, dry pea improves WUE of winter wheat compared with other crops (Anderson, 2009a), whereas Copeland *et al.* (1993) found that soybean did not improve WUE of corn.

Other studies have also shown that legumes can vary in their effect on following crops. For example, Praveen-Kumar *et al.* (1997) found that both water- and N-use efficiency of pearl millet (*Pennisetum glaucum* L.) were higher following cluster bean (*Cymopsis tetragonoloba* (L.) Tauber) than mung bean (*Vigna radiate* (L.) R. Wilczek).

4. Dry Pea Alters the Relationship Between Corn Density and Grain Yield

One of the benefits of genetic improvement in corn is increased tolerance to density stress (Tollenaar *et al.*, 2006). Corn yields more at higher densities due to this improved tolerance. Because dry pea improves tolerance to weed interference, we speculated that dry pea may also improve corn yield at higher plant densities. To test this hypothesis, we compared corn yield at five densities from 45,000 to 73,000 plants/ha at intervals of 7000 plants, planted into stubble of dry pea, soybean, and spring wheat grown the preceding year. The customary density used by producers in this region ranges from 66,000 to 73,000 plants/ha. Corn was grown with best management practices in weed-free conditions.

Following soybean or spring wheat, corn yielded the highest at 73,000 plants/ha, with a gradual increase in yield with increasing plant densities (Fig. 5). However, a surprising trend occurred when corn followed dry pea; corn yielded the highest at 52,000 plants/ha, or with 21,000 less plants than when following soybean or spring wheat. Yields ranged from 6500 to 9800 kg/ha across the 3 years of the study, but yield trends among preceding crops were consistent across years. Seed cost is a major input of producers; this change in optimum corn density following dry pea could reduce seed cost more than $70/ha.

We are unsure why dry pea improved corn yield at low plant densities compared with soybean and spring wheat, but it may involve corn productivity as affected by plant spatial arrangement (Lindquist *et al.*, 1994). The 52,000 plant density resulted in corn plants being equally spaced within the row and between rows (row spacing was 50 cm). Bullock *et al.* (1988) found that corn grown in equidistant plant spacing yielded more grain per unit land area than when grown in conventional plant-spacing patterns. Also, Watkinson (1980) reported that efficiency of resource capture and use is highest when crop plants are equally spaced. Dry pea may have further enhanced resource-use efficiency, thus reducing the need for more plants.

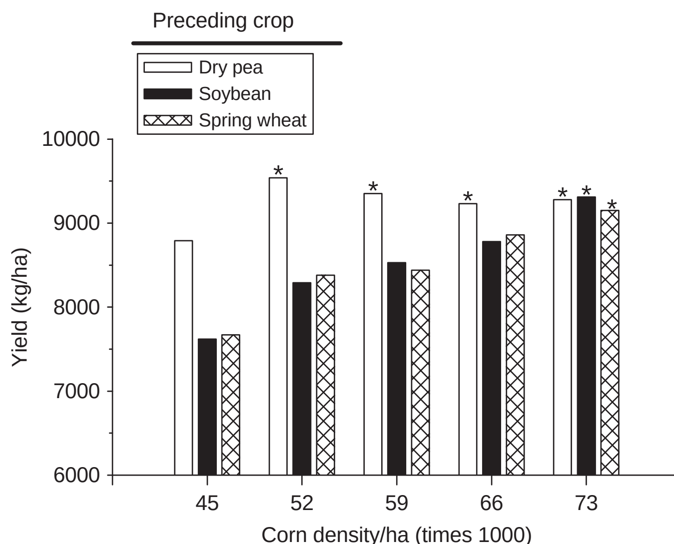


Figure 5 Corn grain yield as affected by preceding crop and corn density. Data averaged across 3 years; bars with an asterisk do not differ significantly from the highest yielding treatment (corn at 52,000 plants/ha following dry pea) based on Fischer's Protected LSD (0.05) (R. L. Anderson, 2011, research in progress).

5. Possible Causes of Synergism Among Crops

Several possible factors could be involved in crop synergism, such as changes in nutrient and water supply (Hobbs, 2007), suppression of pest infestations (Kirkegaard *et al.*, 2008), or release of growth-promoting substances (Anaya, 1999). The microbial community and microbial infestations of the crop also change with crop diversity (Fyson and Oaks, 1990; Turco *et al.*, 1990). One microbial species mentioned often with the rotation effect is mycorrhizae, which improves nutrient and water absorption by plants (Auge, 2004; Ryan and Graham, 2002). To gain insight with the possible cause of synergism, we conducted additional studies that focused on the interaction between dry pea and corn.

5.1. Dry pea does not affect corn growth, development, or nutrient concentration

In the corn density study described above (see Section 4), we monitored growth and development of corn planted after dry pea and soybean (Anderson, 2009b). Plant height and development of designated plants were recorded at the 3-leaf, 6-leaf, 9-leaf, 12-leaf, and silking stages in

corn planted at two densities, 52,000 and 73,000 plants/ha. We also measured concentration of N, P, Zn, and Cu in corn seedlings at the 6-leaf stage. The N concentration may indicate if N availability varies among preceding crops (Przednowek *et al.*, 2004), whereas increased P, Zn, and Cu concentrations may reflect greater colonization of mycorrhizae due to preceding crop (Hamel, 2004; Lambert *et al.*, 1979). Nutrient concentrations were measured at the 6-leaf stage before in-crop N fertilizer was applied. Weeds were controlled with herbicides to eliminate weed interference.

Averaged across the two plant densities, corn yielded 8% more following dry pea compared with soybean. Yet, we detected no differences in corn development, plant height, or nutrient concentration whether corn followed dry pea or soybean (data not shown). Dry pea did not affect capacity (plant size) of corn to increase grain yield. Apparently, factors other than the parameters we measured are involved in dry pea synergism with corn.

Tollenaar and Lee (2002), reviewing the reasons for improved corn yields across time, found that higher yields are related to improved tolerance to stresses such as weed interference, low soil N, and drought, and that the mechanism of tolerance is physiological. We speculate that dry pea synergism involves a change in corn physiology that improves growth efficiency.

5.2. Dry pea synergism to corn persists for 2 years

We also wondered if the favorable impact of dry pea on corn would persist for a second season. Wright (1990) reported that dry pea improved small grain yield for 2 years. In the first year, dry pea increased barley yield 21% compared with continuous barley. In the following year, spring wheat yielded 12% more following the dry pea–barley sequence compared with the barley–barley sequence. Crookston *et al.* (1991) found a similar trend with soybean where the favorable benefit of corn on soybean yield also persisted for 2 years. In contrast, the favorable effect of soybean on corn yield lasted only 1 year.

Therefore, we compared corn grain yield as affected by crop sequences and foxtail millet interference. Dry pea, soybean, and corn were grown in the first year, soybean in all treatments in the second year, and corn in all sequences in the third year. Foxtail millet was grown in corn only during the third year, with each plot split into weed-free and weed-infested subplots.

Even in the second year after dry pea was grown, corn was more tolerant to weed interference. Corn yielded 4500 kg/ha in the dry pea–soybean sequence when foxtail millet was present, but less than 3200 kg/ha following the soybean–soybean and corn–soybean sequences (Fig. 6). Yield loss due to weed interference following the dry pea–soybean sequence was 45%, whereas yield loss following the other sequences was greater than 60%. Synergism occurred in weed-free conditions also, as corn yielded 8% more in the dry pea–soybean–corn sequence than the corn–soybean–corn sequence.

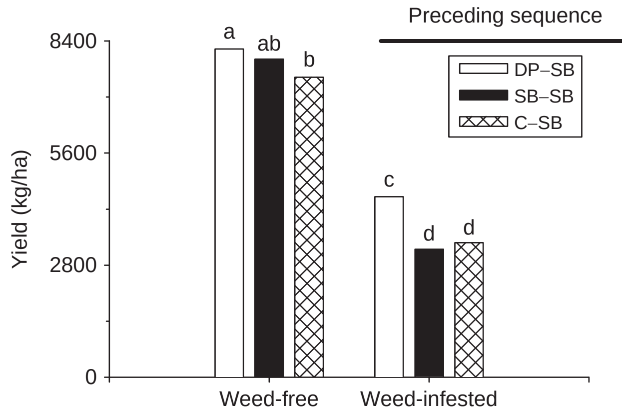


Figure 6 Persistence of dry pea effect on corn yield and tolerance to foxtail millet interference. Fresh weight of foxtail millet 7 weeks after emergence was 1020 ± 77 g/m^2, averaged across all sequences. Grain yield data averaged across 2 years; bars with the same letter are not significantly different based on Fischer's Protected LSD (0.05). DP, dry pea; SB, soybean; C, corn (R. L. Anderson, research in progress).

5.3. Dry pea synergism to corn is greater in low-yielding environments

Tollenaar and Wu (1999) noted that corn is more tolerant of stress because of improved resource-use efficiency, but that this response is frequently only evident under stress conditions. To see if synergism among crops was more pronounced in stress (low-yielding) environments, we compared a uniform treatment of corn following dry pea and soybean that was present in several studies across seven different years. Our comparison involved corn grown at 66,000 plants/ha following dry pea and soybean; plots were maintained weed-free. Corn yielded 11% more following dry pea compared with soybean averaged across the 7 years. But, yield gain due to dry pea was higher in low-yielding years (Fig. 7). Corn yielded 4–5% more following dry pea when yield was greater than 9000 kg/ha; in contrast, yield gain ranged from 14% to 22% when yields were less than 6500 kg/ha.

5.4. Biological factors that may be involved in dry pea synergism with corn

Because corn height and development did not change with preceding crop (see Section 5.1), we believe that dry pea induces a change in efficiency to improve corn yields. This change likely involves corn physiology, as Tollenaar and Lee (2002) reported that increased stress tolerance in corn involves a physiological mechanism.

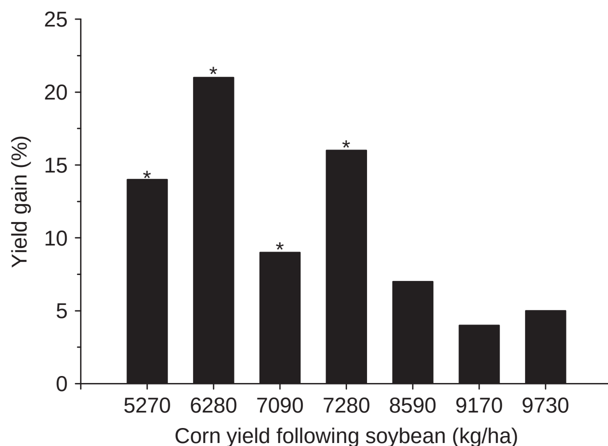


Figure 7 **Yield gain in corn comparing dry pea to soybean as preceding crops, as affected by yield environment. Corn was grown in weed-free conditions in seven different years. Bars with an asterisk differ from the control (soybean as a preceding crop) based on 0.05 level of probability. (Adapted from Anderson, 2007, 2008, 2009b.)**

We also reasoned that synergism between dry pea and corn may involve changes in the microbial community because of its persistence across time (Fig. 6). One possible microbial change due to dry pea involves rhizobacteria (Lupwayi and Kennedy, 2007). Examining the beneficial effect of dry pea on spring wheat yield, Lupwayi *et al.* (2004) found that density of rhizobacteria on spring wheat roots was 700-fold higher when dry pea was the preceding crop compared with wheat. Similarly, Riggs *et al.* (2001) showed that corn yield increased with higher densities of rhizobacteria on its roots. Rhizobacteria confer numerous benefits on its host plant, such as increasing crop tolerance to drought stress (Dobbelaere *et al.*, 2003) and improving photosynthesis efficiency (Peng *et al.*, 2002). Rhizobacteria also improve plant growth by producing growth-promoting substances, suppressing plant pathogens, and increasing nutrient uptake (Sturz *et al.*, 2000). Rhizobacteria can also enhance mycorrhizae colonization of crop roots (Hoffman and Carroll, 1995).

Yet, attempting to identify one biological factor may distort understanding the cause of synergism between crops. A difficulty with relating a specific microbial species to a crop response is the extensive diversity of organisms present in soil and the plethora of interacting processes (Andren *et al.*, 2008; Hooper *et al.*, 2005). Only a small fraction of soil organisms have been identified, which inherently limits our scope in explaining crop response. An example of this difficulty occurred with the study involving rhizobacteria density when wheat followed dry pea (Lupwayi *et al.*, 2004). In this multisite, multiyear study, the authors found that correlation between yield gain and rhizobacteria density varied considerably with climatic conditions and soil type. They speculated that other factors were also involved when dry pea improved spring wheat yield.

Other agronomic disciplines have also noted difficulty in explaining crop interactions. Kirkegaard *et al.* (2008), reviewing impact of crop diversity on root diseases, found that inexplicable rotation effects often confounded the impact of known factors with beneficial crop sequences. Passioura (2002), assessing crop response to growth-promoting compounds in soil, found that interactions among multiple compounds were extremely difficult to understand and predict. He questioned the approach of focusing on one or two compounds to explain a biological response. Stevenson and van Kessel (1996) found that changes in N dynamics accounted for only 8% of the yield gain in wheat following dry pea; the remaining 92% of the yield benefit was attributed to unexplained rotational effects.

Arshad and Frankenberger (1998), noting the complex interaction among growth-promoting substances in soil, suggested that crop response may involve a balance or ratio of several compounds. A similar perspective has been suggested for biochemical interactions among crops (Anaya, 1999; Batish *et al*., 2006). We agree with this perspective and suggest that synergism among crops likely involves several biological factors.

The difficulty in identifying the cause of beneficial crop interactions was demonstrated by Crookston and associates, who conducted a series of studies to explain the rotation effect with corn and soybean (Crookston, 1995). After testing several factors, such as changes in N and P cycling, soil water level, root diseases, allelopathy from crop residues, mycorrhizae colonization, and crop root growth, they finally concluded that the cause of the rotation effect may never be identified. They then shifted their research focus to enhancing the rotation effect with cultural management.

Because of complexity in soil biology, we may not be able to identify a specific cause for crop synergism. Yet, we have recognized trends that can guide management decisions. Dry pea and corn are synergistic to following crops. But, synergism among crops may be rare; we found that only 2 of 11 crops tested were synergistic. Synergism is also related to the crops in sequence. For example, corn is synergistic to proso millet and winter wheat (Anderson, 2005a) but not to sorghum (*Sorghum bicolor* (L.) Moench) (Peterson *et al*., 1990; Schmidt and Frey, 1988). Another example of this specificity among crops occurs with corn synergism to winter wheat and proso millet (Baumhardt and Anderson, 2006). Corn improved WUE of proso millet in a winter wheat–corn–proso millet (W–C–M) rotation, but not when fallow (F) was added to the rotation (W–C–M–F). WUE of proso millet did not differ in the winter wheat–proso millet (W–M), W–M–F, and W–C–M–F rotations. Yet, corn improved WUE of winter wheat in the W–C–F and W–C–M–F rotations which include fallow (Fig. 1). We also suggest, based on our trends (Fig. 7) and observations by Tollenaar and Wu (1999), that synergism may be more favorable in drier regions where stress is common.

6. Benefits of Synergism for Crop Production

Even if the cause of synergism is not known, measuring WUE of crops as affected by the preceding crop may provide a method to identify potential synergistic sequences. The WUE approach is appropriate because a crop integrates the multiple factors of soil biology. After identifying synergistic sequences, production systems could be devised that include these favorable sequences to improve production efficiency.

6.1. Increasing yields without increasing inputs

Synergistic sequences can improve grain yields with the same resource inputs as shown with winter wheat and corn (Figs. 1–3). The benefit of synergism is especially prominent in the semiarid Great Plains. Prior to the development of no-till, the conventional rotation in the Great Plains was winter W–F). A successful no-till rotation in the region is dry pea–winter wheat–corn–proso millet (P–W–C–M; Beck, 2010). Producers have found that yield potential of winter wheat is more than doubled in P–W–C–M (Anderson, 2005c.) Winter wheat rarely yields more than 2650 kg/ha with W–F; in contrast, wheat yields can exceed 5400 kg/ha during favorable years in P–W–C–M. A similar change in yield potential of proso millet also occurs in this rotation. This doubling of yield potential of winter wheat and proso millet, however, has not been observed in no-till rotations without synergistic sequences, such as W–M or W–M–S–F. Part of the yield gain in P–W–C–M can be attributed to improved water relations with no-till, but winter wheat and proso millet yields are 35% to 50% higher than expected based on water and nutrient supply. We believe that synergism due to dry pea and corn is increasing yields of winter wheat and proso millet by improving water- and nutrient-use efficiency.

Because of the success with P–W–C–M, producers are asking if rotations could be designed where all sequences are synergistic. Because synergistic sequences are rare, we initially questioned whether synergism could be extended to the rotation level. But cover crops may provide an option. Two synergistic sequences are present in P–W–C–M (Fig. 8). Winter wheat is not synergistic to corn (Schneekloth *et al.*, 1991), but Kumar *et al.* (2004) found that hairy vetch (*Vicia villosa* Roth), grown as a cover crop, improved stress tolerance in tomato (*Solanum lycopersicum* L.). If a synergistic cover crop existed for corn, productivity of P–W–C–M may be further enhanced by inserting this cover crop between winter wheat and corn (Fig. 8). Biederbeck *et al.* (2005) reported that short intervals of growth with cover crops were sufficient to induce favorable microbial changes in soil.

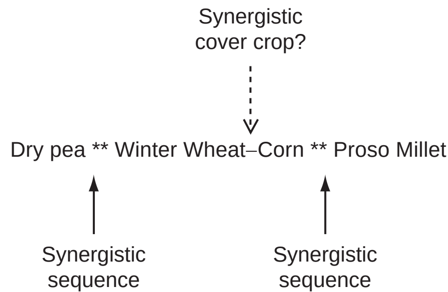


Figure 8 A rotation used in the Great Plains that includes synergistic sequences. Adding a synergistic cover crop between winter wheat and corn may further enhance productivity of this rotation.

Weed management can also benefit from synergistic sequences. Because of crop diversity and no-till, producers can manage weeds with an ecological approach that integrates cultural tactics disruptive of weed population dynamics with herbicide use (Anderson, 2005b). Weed community density declines across time such that herbicides are not needed in some crops. Producers control weeds with 50% less herbicides compared with conventional weed management. Synergism among crops will enhance this approach to weed management by reducing impact of weed escapes and low-density infestations on crop yield.

6.2. Achieving sustainable cropping systems

Land productivity in the United States has increased dramatically because of scientific advancements (Egli, 2008). Deleterious environmental impacts, however, have stimulated questions about long-term sustainability of our current system (Brummer, 1998; Miller, 2008). Energy issues are also a concern because energy is used to produce agricultural chemicals (Kirschenmann, 2007). Thus, producers and scientists are seeking sustainable systems that not only improve productivity and economics but also restore soil health and use resources more efficiently.

To achieve sustainability, Kirschenmann (2010) suggested designing more complex production systems to accentuate biological synergies inherent in multispecies rotations. Similarly, Watt *et al.* (2006) noted that in Australia, major gains in crop productivity result from synergistic interactions among many factors working together, but seldom when management emphasizes one factor. Soil biologists are pursuing a synergy approach, examining rotation designs with complementary crops to increase beneficial

microfloras in soil and improve crop production (Peters *et al.*, 2003; Sturz and Christie, 2003; Sturz and Nowak, 2000).

Synergistic crop sequences can contribute to sustainable systems. For example, synergism in P–W–C–M enabled producers in the semiarid Great Plains to eliminate 12- to 14-month fallow intervals, and thus achieve sustainability in a drought-prone climate (Anderson, 2005c). The conventional rotation in this region, W–F, is extremely damaging to soil health; more than 60% of the original organic matter in soil has been lost (Bowman *et al.*, 1990). Producers use fallow to adapt to limited and erratic precipitation, but improved water relations with no-till enables producers to crop more frequently before fallowing again. Producers tried rotations without fallow, such as winter wheat–proso millet, but these rotations often failed due to lack of water and low WUE (Anderson, 2009a). Rotations such as W–C–M–F are productive and economical, but the 12-month fallow interval minimizes restoration of soil health.

The P–W–C–M rotation, because of its synergistic improvement of WUE, enables producers to crop successfully without fallow, thus accruing both favorable net returns and restoration of soil health. Organic matter levels in soil have increased 37% in 12 years compared with W–F (Sherrold *et al.*, 2003), whereas soil porosity (Shaver *et al.*, 2002) and aggregate stability (Wright and Anderson, 2000) have also improved. One reason why soil health is being restored with P–W–C–M is that land productivity is twice that of W–F (Anderson, 2009a); the increased plant biomass added to soil accelerates soil restoration (Shaver *et al.*, 2003).

Resources are also used more efficiently. Precipitation use is almost twofold higher with P–W–C–M compared with W–F (Anderson, 2005c; Farahani *et al.*, 1998). N cycling is more effective; nitrate quantities in the soil profile are 50% lower in P–W–C–M because more nitrates are used by crops (Anderson, 2009a). Nitrate accumulation and leaching in soil are especially prevalent during 12- to 14-month fallow intervals. Also, P concentration in winter wheat is 15–30% higher in winter wheat following dry pea compared with any rotation where a 12- to 14-month fallow precedes winter wheat (Bowman and Halvorson, 1997).

Hobbs (2007) noted that no-till practices and crop residue preservation on the soil surface have started a cycle of soil regeneration in the drier regions of the world. He suggested that the next step of advancement toward sustainable agriculture is to integrate crop diversity with no-till. Designing rotations to include synergistic sequences will help achieve this advancement and may further improve land productivity without compromising conservation of natural resources, especially in regions with limited resources and precipitation. If synergistic sequences can help eliminate long fallow intervals, soil restoration with no-till and crop diversity will be accelerated.

REFERENCES

Anaya, A. L. (1999). Allelopathy as a tool in the management of biotic resources in agroecosystems. *Crit. Rev. Plant Sci.* **18,** 697–739.

Anderson, R. L. (2005a). Are some crops synergistic to following crops? *Agron. J.* **97,** 7–10.

Anderson, R. L. (2005b). A multi-tactic approach to manage weed population dynamics in crop rotations. *Agron. J.* **97,** 1579–1583.

Anderson, R. L. (2005c). Improving sustainability of cropping systems in the central Great Plains. *J. Sustain. Agric.* **26,** 97–114.

Anderson, R. L. (2007). A changing perspective with weed management in semi-arid cropping systems. *Ann. Arid Zone* **46,** 1–15.

Anderson, R. L. (2008). Crop sequencing can improve corn tolerance to weeds. *West. Soc. Weed Sci. Res. Rep.* 79–80, WSWS, Las Cruces, NM.

Anderson, R. L. (2009a). Rotation design: A key factor for sustainable crop production in a semiarid climate. *In* "Organic Farming, Pest Control and Remediation of Soil Pollutants" (E. Lichthouse, Ed.), pp. 107–121. Springer Publishing, Secaucus, NJ.

Anderson, R. L. (2009b). Pea synergism to corn is not related to seedling growth. *West. Soc. Weed Sci. Res. Rep.* 102–103, WSWS, Las Cruces, NM.

Anderson, R. L. (2009c). Impact of preceding crop and cultural practices on rye growth in winter wheat. *Weed Technol.* **23,** 564–568.

Anderson, R. L. (2010). Dry pea improves winter wheat tolerance to wild rye. *West. Soc. Weed Sci. Res. Rep.* 115–116WSWS, Las Cruces, NM.

Anderson, R. L. (2011). Research in progress.

Anderson, R. L., Bowman, R. A., Nielsen, D. C., Vigil, M. F., Aiken, R. M., and Benjamin, J. G. (1999). Alternative crop rotations for the central Great Plains. *J. Prod. Agric.* **12,** 95–99.

Andren, O., Kirchmann, H., Katterer, T., Magid, J., Paul, E. A., and Coleman, D. C. (2008). Visions of a more precise soil biology. *Eur. J. Soil Sci.* **59,** 380–390.

Angus, J. F., and Van Herwaarden, A. F. (2001). Increasing water use and water use efficiency in dryland winter wheat. *Agron. J.* **93,** 290–298.

Arshad, M., and Frankenberger, W. T. Jr. (1998). Plant growth-regulating substances in the rhizosphere: Microbial production and functions. *Adv. Agron.* **62,** 45–151.

Auge, R. M. (2004). Arbuscular mycorrhizae and soil/plant relations. *Can. J. Plant Sci.* **84,** 373–381.

Batish, D. R., Singh, H. P., Kohli, R. K., and Dawra, G. P. (2006). Potential of allelopathy and allelochemicals for weed management. *In* "Handbook of Sustainable Weed Management" (H. P. Singh, D. R. Batish, and R. K. Kohli, Eds.), pp. 209–256. Food Product Press, New York.

Baumhardt, R. L., and Anderson, R. L. (2006). Crop choices and rotation principles. *In* "Dryland Agriculture" (G. A. Peterson, P. W. Unger, and W. A. Payne, Eds.), *Agron. Monog.*, **23,** pp. 113–139. American Society of Agronomy, Madison, WI.

Beck, D. L. (2010). Successful no-till for the Central and Northern Plains. Dakota Lakes Research Farm, http://www.dakotalakes.com, Accessed November 12 2010.

Biederbeck, V. O., Zentner, R. P., and Campbell, C. A. (2005). Soil microbial populations and activities as influenced by legume green fallow in a semiarid climate. *Soil Biol. Biochem.* **37,** 1775–1784.

Bowman, R. A., and Halvorson, A. D. (1997). Crop rotation and tillage effects on phosphorus distribution in the central Great Plains. *Soil Sci. Soc. Am. J.* **61,** 1418–1422.

Bowman, R. A., Reeder, J. D., and Lober, L. W. (1990). Changes in soil properties after 3, 20, and 60 years of cultivation. *Soil Sci.* **150,** 516–522.

Brummer, E. C. (1998). Diversity, stability, and sustainable American agriculture. *Agron. J.* **90,** 1–2.

Bullock, D. G., Nielsen, R. L., and Nyquist, W. E. (1988). A growth analysis comparison of corn grown in conventional and equidistant plant spacing. *Crop Sci.* **28,** 254–258.

Cayci, G., Heng, L. K., Oztruk, H. S., Suerek, D., Kutuk, C., and Saglam, M. (2009). Crop yield and water use efficiency in a semi-arid region of Turkey. *Soil Tillage Res.* **103,** 65–72.

Cook, R. J. (1990). Diseases caused by root-infecting pathogens in dryland agriculture. *Adv. Soil Sci.* **13,** 215–239.

Copeland, P. J., and Crookston, R. K. (1992). Crop sequence affects nutrient composition of corn and soybean grown under high fertility. *Agron. J.* **84,** 503–509.

Copeland, P. J., Allmaras, R. R., Crookston, R. K., and Nelson, W. W. (1993). Corn-soybean rotation effects on soil water depletion. *Agron. J.* **85,** 203–210.

Crookston, R. K. (1995). The rotation effect in corn. *In* "Proceedings 50th Annual Corn Sorghum Research Conference" (D. Wilkerson, Ed.), pp. 201–215. American Seed Trade Association, Alexandria, Virginia.

Crookston, R. K., Kurle, J. E., Copeland, P. J., Ford, J. H., and Lueschen, W. E. (1991). Rotational cropping sequence affects yield of corn and soybean. *Agron. J.* **83,** 108–113.

Dobbelaere, S., Vanderleyden, J., and Okon, Y. (2003). Plant growth-promoting effects of diazotrophs in the rhizosphere. *Crit. Rev. Plant Sci.* **22,** 107–149.

Egli, D. B. (2008). Comparison of corn and soybean yields in the United States: Historical trends and future prospects. *Agron. J.* **100**(Suppl.), 79–88.

Farahani, H. J., Peterson, G. A., and Westfall, D. G. (1998). Dryland cropping intensification: A fundamental solution to efficient use of precipitation. *Adv. Agron.* **64,** 197–223.

Fyson, A., and Oaks, A. (1990). Growth promotion of maize by legume soils. *Plant Soil* **122,** 259–266.

Hamel, C. (2004). Impact of arbuscular mycorrhizal fungi on N and P cycling in the root zone. *Can. J. Soil Sci.* **84,** 383–395.

Hobbs, P. R. (2007). Conservation agriculture: What it is and why is it important for future sustainable food production? *J. Agric. Sci.* **145,** 127–137.

Hoffman, C. A., and Carroll, C. R. (1995). Can we sustain the biological basis of agriculture? *Annu. Rev. Ecol. Syst.* **26,** 69–92.

Hooper, D. U., Cahpin, F. S., Ewel, J. J., *et al.* (2005). Effects of biodiversity on ecosystem functioning: A consensus of current knowledge. *Ecol. Monogr.* **75,** 3–35.

Kirkegaard, J. O., Christen, O., Krupinsky, J., and Layell, D. (2008). Break crops benefits in temperate wheat production. *Field Crop Res.* **107,** 185–195.

Kirschenmann, F. L. (2007). Potential for a new generation of biodiversity in agroecosystems of the future. *Agron. J.* **99,** 373–376.

Kirschenmann, F. L. (2010). Alternative agriculture in an energy- and resource-depleting future. *Renew. Agric. Food Syst.* **25,** 85–89.

Kruger, G. R., Johnson, W. G., Weller, S. R., *et al.* (2009). U.S. grower views on problematic weeds and changes in weed pressure in glyphosate-resistant corn, cotton, and soybean cropping systems. *Weed Technol.* **23,** 162–166.

Krupinsky, J. M., Bailey, K. L., McMullen, M. P., Gossen, B. D., and Turkington, T. K. (2002). Managing plant disease risk with diversified cropping systems. *Agron. J.* **94,** 198–209.

Kumar, V., Mills, D. J., Anderson, J. D., and Mattoo, A. K. (2004). An alternative agriculture system is defined by a distinct expression profile of select gene transcripts and proteins. *Proc. Natl. Acad. Sci. USA* **101,** 10535–10540.

Lafond, G. P., May, W. E., Stevenson, F. C., and Derksen, D. A. (2006). Effects of tillage systems and rotations on crop production for a thin Black Chernozem in the Canadian Prairies. *Soil Tillage Res.* **89,** 232–245.

Lambert, D. H., Baker, D. E., and Cole, H. Jr. (1979). The role of mycorrhizae in the interactions of phosphorus with zinc, copper, and other elements. *Soil Sci. Soc. Am. J.* **43,** 976–980.

Lindquist, J. L., Rhode, D., Puettmann, K. J., and Maxwell, B. D. (1994). The influence of plant population spatial arrangement on individual plant yield. *Ecol. Appl.* **4,** 518–524.
Lupwayi, N. Z., and Kennedy, A. C. (2007). Grain legumes in northern Great Plains: Impacts on selected biological soil processes. *Agron. J.* **99,** 1700–1709.
Lupwayi, N. Z., Clayton, G. W., Hanson, K. G., Rice, W. A., and Biederbeck, V. O. (2004). Endophytic rhizobia in barley, wheat, and canola roots. *Can. J. Plant Sci.* **84,** 37–45.
Miller, F. P. (2008). After 10,000 years of agriculture, whither agronomy? *Agron. J.* **100,** 22–34.
Moyer, J. R., Blackshaw, R. E., Doram, R. C., Huang, H. C., and Entz, M. H. (2004). Effect of previous crop and herbicides on weed growth and wheat yield. *Can. J. Plant Sci.* **85,** 735–746.
Passioura, J. B. (2002). Soil conditions and plant growth. *Plant Cell Environ.* **25,** 311–318.
Peng, S., Biswas, J. C., Ladha Adha, J. K., Cyaneshwar, P., and Chen, Y. (2002). Influence of rhizobial inoculation on photosynthesis and grain yield of rice. *Agron. J.* **94,** 925–929.
Peters, R. D., Sturz, A. V., Carter, M. R., and Sanderson, J. B. (2003). Developing disease-suppressive soils through crop rotation and tillage management practices. *Soil Tillage Res.* **72,** 181–192.
Peterson, G. A., and Westfall, D. G. (2004). Managing precipitation use in sustainable dryland agroecosystems. *Ann. Appl. Biol.* **144,** 127–138.
Peterson, T. A., Shapiro, C. A., and Flowerday, A. D. (1990). Rainfall and previous crop effects on crop yields. *Am. J. Altern. Agric.* **5,** 33–37.
Porter, P. M., Crookston, R. K., Ford, J. H., Huggins, D. R., and Lueschen, W. E. (1997). Interrupting yield depression in monoculture corn: Comparative effectiveness of grasses and dicots. *Agron. J.* **89,** 247–250.
Praveen-Kumar, Aggarwal, R. K., and Power, J. F. (1997). Cropping systems: Effects on soil quality indicators and yield of pearl millet in an arid region. *Am. J. Altern. Agric.* **12,** 178–184.
Przednowek, D. W., Entz, M. H., Irvine, B., Flaten, D. N., and Thiessen-Martens, J. R. (2004). Rotational yield and apparent N benefits of grain legumes in southern Manitoba. *Can. J. Plant Sci.* **84,** 1093–1096.
Riggs, P. J., Chelius, M. K., Iniguez, A. L., Kaeppler, S. M., and Triplett, E. W. (2001). Enhanced maize productivity by inoculation with diazotrophic bacteria. *Aust. J. Plant Physiol.* **28,** 829–836.
Ryan, M. H., and Graham, J. H. (2002). Is there a role for abuscular mycorrhizal fungi in production agriculture? *Plant Soil* **244,** 263–271.
Schmidt, G., and Frey, E. (1988). Crop rotation effects in northern Ghana. *In* "Proceedings of Challenges in Dryland Agriculture Conference" (P. W. Unger, *et al.*, Eds.), pp. 775–777. Texas Agric. Exp. Stn., College Station, Bushland, TX.
Schneekloth, J. P., Klocke, N. L., Hergert, G. W., Martin, D. L., and Clark, R. T. (1991). Crop rotations with full and limited irrigation and dryland management. *Trans. ASAE* **34,** 2372–2380.
Shaver, T. M., Peterson, G. A., Ahuja, L. R., Westfall, D. G., Sherrold, L. A., and Dunn, G. (2002). Surface soil physical properties after twelve years of dryland no-till management. *Soil Sci. Soc. Am. J.* **66,** 1296–1303.
Shaver, T. M., Peterson, G. A., and Sherrold, L. A. (2003). Cropping intensification in dryland systems improves soil physical properties: Regression relations. *Geoderma* **116,** 149–164.
Sherrold, L. A., Peterson, G. A., Westfall, D. G., and Ahuja, L. R. (2003). Cropping intensity enhances soil organic carbon and nitrogen in a no-till agroecosystem. *Soil Sci. Soc. Am. J.* **67,** 1533–1543.
Stevenson, F. C., and van Kessel, C. (1996). The nitrogen and non-nitrogen rotation benefits of pea to succeeding crops. *Can. J. Plant Sci.* **76,** 735–745.

Sturz, A. V., and Christie, B. R. (2003). Beneficial microbial allelopathies in the root zone: The management of soil quality and plant disease with rhizobacteria. *Soil Tillage Res.* **72,** 107–123.

Sturz, A. V., and Nowak, J. (2000). Endophytic communities of rhizobacteria and the strategies required to create yield enhancing associations with crops. *Appl. Soil Ecol.* **15,** 183–190.

Sturz, A. V., Christie, B. R., and Nowak, J. (2000). Bacterial endophytes: Potential role in developing sustainable systems of crop production. *Crit. Rev. Plant Sci.* **19,** 1–30.

Tollenaar, M., and Lee, E. A. (2002). Yield potential, yield stability, and stress tolerance in maize. *Field Crops Res.* **75,** 161–169.

Tollenaar, M., and Wu, J. (1999). Yield improvement in temperate maize is attributable to greater stress tolerance. *Crop Sci.* **39,** 1597–1604.

Tollenaar, M., Deen, W., Echarte, L., and Liu, W. (2006). Effect of crowding stress on dry matter accumulation and harvest index in maize. *Agron. J.* **98,** 930–937.

Turco, R. F., Bishcoff, M., Breakwell, D. P., and Griffith, D. R. (1990). Contribution of soil-borne bacteria to the rotation effect in corn. *Plant Soil* **122,** 115–120.

Vereijken, R. (2002). Transition to multifunctional land use and agriculture. *Neth. J. Agric. Sci.* **50,** 171–179.

Vetsch, J. A., and Randall, G. W. (2000). Enhancing no-tillage systems for corn with starter fertilizer, row cleaners, and nitrogen placement factors. *Agron. J.* **92,** 309–315.

Watkinson, A. R. (1980). Density-dependence in single-species populations of plant. *J. Theor. Biol.* **83,** 345–357.

Watt, M., Kirkegaard, J. A., and Passioura, J. B. (2006). Rhizosphere biology and crop productivity—A review. *Aust. J. Soil Res.* **44,** 299–317.

White, A. D., Lyon, D. J., Mallory-Smith, C., Medlin, C. R., and Yenish, J. P. (2006). Feral rye (*Secale cereale*) in agricultural production systems. *Weed Technol.* **20,** 815–823.

Wright, A. T. (1990). Yield effect of pulses on subsequent cereal crops in the northern plains. *Can. J. Plant Sci.* **70,** 1023–1032.

Wright, S. F., and Anderson, R. L. (2000). Aggregate stability and glomalin in alternative crop rotations for the central Great Plains. *Biol. Fertil. Soils* **31,** 249–253.

Index